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THERMO-OPTIC BEHAVIOUR OF SOLIDS

V. Alkali Halides

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1. Introduction

The halides of the alkali metals form a class of crystalline solids which, on account of the simplicity of their structure, have been the subject of a great many investigations, both theoretical and experimental. In particular, we have a wealth of data on their refractive indices and dispersion. Besides, the work of Hilsch and Pohl (1930) and of Schneider and O'Bryan (1937) have revealed the actual existence of a number of dispersion frequencies in the remote ultra-violet, and in two particular cases, *viz.*, potassium iodide and rubidium bromide, the actual shifting down of these frequencies towards longer wavelengths with rise of temperature has been observed and quantitatively measured (Fesefeldt, 1930). The last mentioned phenomenon is the basis of our theory of thermo-optic behaviour. So far, it had a direct observational basis only for diamond. In this case, although the actual dispersion frequencies have not been observed spectroscopically, the shifts of various other electronic frequencies have been measured, and the proportional rate of change of frequency calculated from these agree with the value for the dispersion frequency deduced from measurements of dn/dt. Fesefeldt's data are therefore of great interest in relation to the present theory as they form a direct confirmation of the ideas developed in it. As will be seen from a later section, it is found that the rate of change of the dispersion frequency calculated from the refractive index data is in agreement with the actually measured value for KI.

With regard to the thermo-optic behaviour of the alkali halides in general, the data are not as plentiful as could be desired. dn/dt has been measured for rock-salt (NaCl), the most familiar of these, between $0{\cdot}185$ and $0{\cdot}671\,\mu$ by Micheli (1902) and from $0{\cdot}589$ to $8{\cdot}85\,\mu$ by Liebreich (1911). For sylvine (KCl), there are data in the visible for wavelengths above $0{\cdot}434\,\mu$ measured by Pulfrich (1892) and in the infra-red by Liebreich (*loc. cit.*) but none at all in the ultra-violet. Among the rest, the following are the only measurements of dn/dt available: for KBr and KI for only

TABLE I

Compound	Reference	Wavelengths for which measurements are available (in microns)
LiF	Gyulai (1927)	0·193 to 0·578
	Hohls (1937)	0·546 to 55·0
	Ramaseshan (1947)	0·436, 0·546, 0·589
NaF	Kublitzky (1934)	0·186 to 0·578
	Hohls (1937)	0·546 to 55·0
KF	Kublitzky (1934)	0·214 to 0·578
RbF	Winchell (1931)	F (0·486), D (0·589), C (0·656)
αCsF	Posnjak and Wyckoff (1922)	F, D, C
βCsF	Winchell (1931)	F, D, C
LiCl		
NaCl*	Martens (1901)	0·185 to 0·589
	Paschen (1908)	0·589 to 15·9
	Rubens and Trowbridge (1897)	9·95 to 17·93
	Rubens and Nichols (1897)	20·57, 22·3
KCl*	Martens (1901)	0·185 to 0·768
	Paschen (1908)	0·589 to 17·68
	Trowbridge (1898)	0·98 to 11·2
	Rubens and Nichols (1897)	20·6, 22·3
RbCl	Sprockhoff (1903)	F, D, C
	Gyulai (1927)	0·193 to 0·577
αCsCl	Winchell (1931)	F, D, C
	Wulff and Schaller (1934)	0·480, 0·546, 0·589, 0·671
	Wulff and Anderson (1935)	0·226 to 0·538
βCsCl	Sprockhoff (1903)	F, D, C
LiBr		
NaBr	Spangenberg (1923)	0·436, 0·447, 0·501, 0·588, 0·608
	Gyulai (1927)	0·206 to 0·615
KBr	Topsoe and Christiansen (1874)	Hγ (0·434), F, D, C
	Sprockhoff (1903)	F, D, C
	Winchell (1931)	F, D, C
	Gyulai (1927)	0·206 to 0·615
	Gundelach (1930)	0·768 to 28·5
	Korth (1933)	14 to 26·7
	Forrest (1942)	0·405 to 0·770
	Ramaseshan (1947)	0·436, 0·546, 0·589
RbBr	Sprockhoff (1903)	F, D, C
	Kublitzky (1934)	0·219 to 0·578
αCsBr	Winchell (1931)	F, D, C
LiI		
NaI		
KI	Topsoe and Christiansen (1874)	F, D, C
	Sprockhoff (1903)	F, D, C
	Winchell (1931)	F, D, C
	Gyulai (1927)	0·254 to 0·615
	Korth (1933)	0·546 to 29·0
RbI	Sprockhoff (1903)	F, D, C
	Kublitzky (1934)	0·253 to 0·578
αCsI	Winchell (1931)	F, D, C
βCsI	Sprockhoff (1903)	F, D, C

* For NaCl and KCl, only a few references are given covering the whole wavelength range. For a fuller list, see Herzfeld and Wolf (1925).

one wavelength, the 5461 Å.U. radiation of mercury (Korth, 1934) and for LiF for λλ 0·546 and 3·5 μ and for NaF for λλ 0·546, 3·5 and 8·5 μ (Hohls, 1937). In this paper, the cases of rocksalt and sylvine have been worked out in detail which lead to some interesting results. Potassium iodide has also been considered somewhat in detail on account of the special considerations mentioned above.

2. Some General Considerations

As has been mentioned in the earlier papers of this series, a prerequisite to the theoretical explanation of the thermo-optic properties of a solid is the derivation of a dispersion formula. For both rocksalt and sylvine, various dispersion formulæ have been suggested (Paschen, 1908; Martens, 1901; Goldhammer, 1913; Herzfeld and Wolf, 1925; Fuchs and Wolf, 1928), while for the other alkali halides none have been proposed to the knowledge of the author. All these formulæ should however be considered empirical, since the dispersion frequencies have been taken only so as to fit the refractive index data and have no experimental basis. Since 1930, the ultra-violet absorption frequencies of all the alkali halides (except LiF) and various other crystals have been determined down to about 1000 Å.U. (Hilsch and Pohl, 1930; Schneider and O'Bryan, 1937). In the infra-red also, the absorption frequencies of most of the alkali halides have been directly determined (Barnes and Czerny, 1931; Barnes, 1932). All the measurements have been listed in Barnes' paper (1932). Apart from their importance in other fields, these measurements both in the ultra-violet and in the infra-red are very valuable since they can be directly incorporated in the dispersion formulæ and thus place these formulæ on a sounder theoretical basis. In the present paper such a calculation has been carried out for rocksalt and potassium iodide, for which such an investigation seemed desirable prior to the calculation of the thermo-optic phenomena. There is no doubt that dispersion formulæ embodying the actual absorption frequencies can be obtained for the other salts as well, for many of which extensive data are available for the refractive indices at various wavelengths. In Table I below, a list of references is given of the various published investigations on the refractive indices of alkali halides. Only those in which refractive indices for at least 3 wavelengths have been measured are included in the list.

An important question that has to be considered in this connection is whether the proper form of the dispersion formula is of the Drude type, *viz.*,

$$n^2 - 1 = \sum_r a_r \lambda_r^2/(\lambda^2 - \lambda_r^2), \qquad (1)$$

or of the Lorentz-Lorenz type, *viz.*,

$$\frac{n^2-1}{n^2+2} = \Sigma_r a_r' \lambda_r'^2/(\lambda^2 - \lambda_r'^2). \quad (2)$$

As has been shown by Herzfeld and Wolf (1925), these two forms are algebraically interconvertible into each other. It is therefore necessary to understand precisely what the significance of the quantities λ_r and λ_r' is in the expressions (1) and (2) respectively. It is obvious that if those in (1) are really the wavelengths corresponding to the dispersion frequencies, those in (2) are not, and *vice versa*. To decide which is true, we have on the one hand, the purely theoretical approach to the problem of the dispersion of crystalline bodies, based on lattice theory and considering the interaction of electromagnetic radiation with the regular array of atoms in the crystal. Such theories have been developed by Ewald (1916) and Born (1918, 1922) and their results show that the resultant expression does not take the Lorentz-Lorenz form, but the $(n^2 - 1)$ form. On the other hand, one could actually compute dispersion formulæ of both types and see in which case the assumed dispersion frequencies agree with the observed absorption frequencies. The alkali halides form suitable materials in which to make such critical calculations.

For rocksalt and sylvine, calculations of this type have already been carried out by Wolf and his collaborators (Herzfeld and Wolf, 1925; Fuchs and Wolf, 1928), although not with this specific purpose. They have obtained dispersion formulæ for these substances both in the Lorentz-Lorenz and the Drude forms. In both cases, four dispersion frequencies are used, one in the infra-red, two in the ultra-violet above 1000 Å.U. and one in the still remote ultra-violet. In Table II, the wavelengths of the frequencies employed in the two forms for both NaCl and KCl are given, together with the actually observed values. These measurements have been made, after the publication of the dispersion formulæ, by Barnes and Czerny (1930) in the infra-red and by Schneider and O'Bryan (1937) in the ultra-violet. It will be seen that the dispersion frequencies used in the Drude form agree remarkably well with the infra-red and the nearest ultra-violet frequency. In fact, even the second ultra-violet dispersion frequency is reasonably correct, since it can be supposed to represent both the second and the third absorption frequencies. No such agreement is found with the Lorentz-Lorenz form. There is thus strong reason to believe that the Drude form is really the more appropriate one for the alkali halides and probably for cubic crystals in general. In this connection, it may be mentioned that the author (1947) has succeeded in constructing a Drude dispersion formula for fluorspar, in which the observed absorption maxima

in the ultra-violet are employed. In view of the above considerations, we shall only make use of the (n^2-1) form of the dispersion formula in the succeeding discussions in this paper.

TABLE II

Wavelengths of the Dispersion Frequencies

Rocksalt			Sylvine		
L–L. Form	Drude form	Observed	L–L. Form	Drude form	Observed
343·9 Å.U.	347 Å.U.		514·6 Å.U.	529·1 Å.U.	
		1000 Å.U.			1000 Å.U.
935·9 ,,	1085 ,,		966·9 ,,	1082·8 ,,	
		1280 ,,			1310 ,,
1543·4 ,,	1584 ,,	1580 ,,	1582·9 ,,	1621·4 ,,	1620 ,,
45·75μ	61·67μ	61·1μ	55·09μ	70·23μ	70·7μ

3. Dispersion Formulae of Rocksalt and Sylvine

As already mentioned, rocksalt is the only alkali halide for which dn/dt measurements are available over the whole spectral range from 0·2 to 9 μ. It will be therefore interesting to apply the theory of thermo-optic behaviour developed by the author (1947 *a*) and consider its various consequences. For this purpose, it is desirable to have an accurate dispersion formula containing the observed frequencies. Such a formula has been constructed by the author and is given below.

Various dispersion formulæ have been suggested for rocksalt which are listed below. They have all been reduced wherever possible to the standard forms

$$n^2-1 \text{ or } \frac{n^2-1}{n^2+2} = C+\sum_r \frac{a_r \lambda^2}{\lambda^2-\lambda_r^2} \tag{3}$$

Paschen (1908)

$$n^2-1 = 0\cdot2807+\frac{0\cdot8397\lambda^2}{\lambda^2-(0\cdot1219)^2}+\frac{0\cdot2098\,\lambda^2}{\lambda^2-(0\cdot1596)^2}+\frac{3\cdot350\,\lambda^2}{\lambda^2-(60\cdot0)^2} \tag{4}$$

Martens (1901)

$$n^2-1 = 0\cdot155992+\frac{0\cdot855461\,\lambda^2}{\lambda^2-(0\cdot110725)^2}+\frac{0\cdot317791\,\lambda^2}{\lambda^2-(0\cdot156320)^2}$$
$$+\frac{1\cdot620760\,\lambda^2}{\lambda^2-(51\cdot2)^2}-0\cdot000309178\,\lambda^2 \tag{5}$$

Herzfeld and Wolf (1925)

$$\frac{n^2-1}{n^2+2}=\frac{0\cdot018619\,\lambda^2}{\lambda^2-(0\cdot03439)^2}+\frac{0\cdot25898\,\lambda^2}{\lambda^2-(0\cdot09359)^2}+\frac{0\cdot029763\,\lambda^2}{\lambda^2-(0\cdot15434)^2}+\frac{0\cdot31207\,\lambda^2}{\lambda^2-(45\cdot75)^2} \tag{6}$$

Fuchs and Wolf (1928)

$$n^2-1=\frac{0\cdot05225\,\lambda^2}{\lambda^2-(0\cdot0347)^2}+\frac{1\cdot0059\,\lambda^2}{\lambda^2-(0\cdot1085)^2}+\frac{0\cdot2713\,\lambda^2}{\lambda^2-(0\cdot1584)^2}+\frac{3\cdot5417\,\lambda^2}{\lambda^2-(61\cdot67)^2} \tag{7}$$

The author's new formula using the observed frewquencies is

$$n^2-1=\frac{0\cdot187895\,\lambda^2}{\lambda^2-(0\cdot0500)^2}+\frac{0\cdot497649\,\lambda^2}{\lambda^2-(0\cdot1000)^2}+\frac{0\cdot384897\,\lambda^2}{\lambda^2-(0\cdot1280)^2}+\frac{0\cdot259500\,\lambda^2}{\lambda^2-(0\cdot1580)^2}+\frac{3\cdot4740\,\lambda^2}{\lambda^2-(61\cdot1)^2} \tag{8}$$

Paschen has suggested many formulæ. The one given here is his latest. It may be mentioned that Paschen was particularly interested in the infra-red, where from $0\cdot6\,\mu$ to nearly $22\,\mu$, his formula fits well, but it is rather poor in the visible and the ultra-violet, as is revealed by a check made by the author. Martens' formula fits his earlier measurements (1901) remarkably well but not so well with his later measurements (1902), which are more accurate, as judged by the fact that only these are given by Martens himself in the Landolt-Bornstein Tables (1923). Herzfeld and Wolf's formula is of the Lorentz-Lorenz type and the dispersion frequencies used in it do not agree with experimental values.. Fuchs and Wolf's formula is perhaps the best suggested so far, in view of the various considerations mentioned earlier. There is however room for improvement in this formula as well. Firstly, the numerical agreement with the refractive index data is not as good as could be expected. Fuchs and Wolf have represented the errors (theoretical—experimental) not in n itself, but in $(n^2-1)/(n^2+2)$, which often comes to 3 units in the fourth decimal place. This means that in (n^2-1) they come to nearly 15 units. Besides, the second and third ultra-violet frequencies have been put together in a single term. In the new formula suggested by the author, the frequencies are all those that have been observed, except the one at 500 Å.U. This stands for a group of frequencies in the very remote ultra-violet, of which no definite further details are known. It is found that the new formula fits the experimental data much better than Fuchs and Wolf's formula, as may be seen from an examination of Table III. Here, the errors in (n^2-1) (theoretical—experimental) are given in units of the fourth decimal place both with the Fuchs-Wolf formula and the

author's formula. It will be seen that with the new formula, the error is scarcely above 5 units, except for the extreme values in the ultra-violet and the infra-red, while in the middle of the table, it is rarely more than 2 units. In the Fuchs-Wolf formula, on the other hand, the errors appear to be systematic, being often above 10 units and sometimes larger than 15 units. The experimental data for comparison have been taken from the tables compiled by Martens (1923) in the Landolt-Bornstein Tables.

TABLE III

Wavelength in microns	Refractive index		(n^2-1) (th.−exp.) × 10^4	
	Experimental	From author's formula	Author's formula	Fuchs-Wolf's formula
0·185467	1·89332	1·89350	+ 7·0	+ 16·2
0·186290	1·88558	1·88555	− 1·1	+ 10·5
0·193583	1·82809	1·82793	− 5·8	+ 0·7
0·19898	1·79580	1·79591	+ 3·8	..
0·20006	1·79016	1·79028	+ 4·2	0·0
0·214439	1·73221	1·73211	− 3·2	+ 8·0
0·219462	1·71711	1·71705	− 2·2	+ 12·4
0·231288	1·68840	1·68835	− 1·8	+ 15·0
0·257304	1·64604	1·64604	0·0	+ 16·5
0·274869	1·62687	1·62692	+ 1·5	+ 18·1
0·340365	1·58601	1·58609	+ 2·4	+ 12·7
0·441568	1·55962	1·55965	+ 1·0	+ 7·5
0·486133	1·55338	1·55340	+ 0·5	+ 4·0
0·546072	1·54745	1·54745	+ 0·1	+ 3·0
0·58932	1·54431	1·54431	0·0	0·0
0·656278	1·54067	1·54067	− 0·1	− 1·7
0·78576	1·53614	1·53615	+ 0·2	− 2·1
0·88396	1·53401	1·53398	− 1·1	− 5·7
1·1786	1·53037	1·53034	− 0·9	− 6·9
4·1252	1·52165	1·52155	− 3·1	− 11·2
8·8398	1·50204	1·50197	− 2·2	− 10·2
12·9650	1·47172	1·47182	+ 3·0	− 5·0
22·3	1·3405	1·3402	− 8·5	− 2·2

For sylvine also, a number of dispersion formulæ have been suggested which are given below.

Paschen (1908)

$$n^2-1=0\cdot200970+\frac{0\cdot700711\,\lambda^2}{\lambda^2-(0\cdot109125)^2}+\frac{0\cdot273286\,\lambda^2}{\lambda^2-(0\cdot159859)^2}+\frac{1\cdot691652\,\lambda^2}{\lambda^2-(57\cdot380)^2} \qquad (9)$$

Martens (1901)

$$n^2-1=0.25841+\frac{0\cdot672011\,\lambda^2}{\lambda^2-(0\cdot115265)^2}+\frac{0\cdot244603\,\lambda^2}{\lambda^2-(0\cdot160730)^2}+\frac{1\cdot93343\,\lambda^2}{\lambda^2-(61\cdot1)^2} \qquad (10)$$

Goldhammer (1913)

$$\frac{n^2-1}{n^2+2} = 0.084232 + \frac{0{\cdot}169065\,\lambda^2}{\lambda^2-(0{\cdot}106673)^2} + \frac{0{\cdot}0281324\,\lambda^2}{\lambda^2-(0{\cdot}157500)^2} + \frac{0{\cdot}232735\,\lambda^2}{\lambda^2-(51{\cdot}009)^2} \tag{11}$$

Herzfeld and Wolf (1925)

$$\frac{n^2-1}{n^2+2} = \frac{0{\cdot}059064\,\lambda^2}{\lambda^2-(0{\cdot}05146)^2} + \frac{0{\cdot}19277\,\lambda^2}{\lambda^2-(0{\cdot}09669)^2} + \frac{0{\cdot}029883\,\lambda^2}{\lambda^2-(0{\cdot}15829)^2} + \frac{0{\cdot}27700}{\lambda^2-(55{\cdot}09)^2} \tag{12}$$

Fuchs and Wolf (1928)

$$n^2-1 = \frac{0{\cdot}15779\,\lambda^2}{\lambda^2-(0{\cdot}05291)^2} + \frac{0{\cdot}78836\,\lambda^2}{\lambda^2-(0{\cdot}10828)^2} + \frac{0{\cdot}22971\,\lambda^2}{\lambda^2-(0{\cdot}16214)^2} + \frac{2{\cdot}6149\,\lambda^2}{\lambda^2-(70{\cdot}23)^2} \tag{13}$$

The comments made on Paschen's and Marten's formulæ for rocksalt also hold in this case. Goldhammer's formula was available to the author only through the paper of Herzfeld and Wolf (*loc. cit.*), who criticise it on the ground that it does not give a reasonable value for the dielectric constant. This, as well as Herzfeld and Wolf's formulæ, are of the Lorentz-Lorenz type. Once again, Fuchs and Wolf's formula is the most acceptable for the same reasons as mentioned before, but the errors are as large as with rocksalt in this case also. The author is of the opinion that the general fit of the dispersion formula can be improved as with rocksalt by using the observed frequencies. This was not however attempted as it was unnecessary for the present investigation, *viz.*, the study of the thermo-optical properties. Measurements of dn/dt for sylvine are available only for wavelengths above $0{\cdot}45\,\mu$ and in this region the exact location of the ultra-violet frequencies is relatively unimportant. Consequently the Fuchs-Wolf formula was used in the calculations.

3. Calculation of the Spectral Variation of dn/dt for Rocksalt and Sylvine

(*a*) *Rocksalt.*—The calculation of dn/dt was carried out in the same way as with the other solids studied earlier. Taking a dispersion formula of the Drude form (Eq. 1) one has

$$2n\,dn/dt = -\gamma(n^2-1) + \Sigma 2a_r\lambda^4\chi_r/(\lambda^2-\lambda_r^2)^2. \tag{14}$$

where

$$\chi_r = d(\log \lambda_r)/dt = -d(\log \nu_r)/dt. \quad (15)$$

The available data for rocksalt are all at 60° C. for which temperature the coefficient of cubical expansion $\gamma = 1{\cdot}20 \times 10^{-4}$ (*International Critical Tables*, Vol. 3, p. 43) from which the first term on the right hand side, *viz.*, the contribution due to change in density can be calculated. It now remains to determine only the χ's of the various frequencies. Now, in the visible and ultra-violet regions, the contribution due to changes in the infra-red frequency is very small. Neglecting this, it is found that the experimental data are fitted with the following values of χ_r:

Fuchs-Wolf formula (Eq. 7):

$$\chi(347\text{ Å}) = 0,\ \chi(1085\text{ Å}) = -9.7 \times 10^{-6},\ \chi(1584\text{ Å}) = 113 \times 10^{-6} \quad (16)$$

Author's formula (Eq. 8):

$$\chi(500\text{ Å}) = 0,\ \chi(1000\text{ Å}) = -33.3 \times 10^{-6},\ \chi(1280\text{ Å}) = 23.5 \times 10^{-6},$$
$$\chi(1580\text{ Å}) = 110 \times 10^{-6}. \quad (17)$$

In Table IV, the experimental values of dn/dt together with the values calculated from the two formulæ are given for a few selected wavelengths. The data up to 0·5893 is due to Micheli (1902) and those in the infra-red to Liebreich (1911). In the infra-red, the calculations have been carried out with the assumption that the χ for the infra-red frequency is 150×10^{-6}. This value is not unreasonable, since it is of the same order as the χ for the first ultra-violet frequency (at 1580 Å) and also as that for the infra-red frequency in fluorspar. Besides, it may be mentioned that the contribution to dn/dt due to the infra-red frequency shift is small even at 8 μ, so that any error in the assumed value of χ is unimportant.

TABLE IV

Wavelength in microns	$dn/dt \times 10^6$		
	From experiment	From author's formula	From Fuchs-Wolf formula
0·2026	+ 29·87	+ 29·5	+ 30·7
0·2145	+ 7·12	+ 6·6	+ 6·3
0·2574	− 21·05	− 19·9	− 20·3
0·3405	− 31·84	− 32·6	− 30·8
0·4680	− 35·66	− 36·5	− 36·6
0·5893	− 37·33	− 37·3	− 36·9
1·6	− 36·64	− 38·6	− 38·6
4·96	− 32·81	− 37·8	− 37·8
6·4	− 32·41	− 37·3	− 37·3
8·85	− 25·23	− 36·1	− 36·1

It may be noticed from the table that in the ultra-violet and visible, the agreement with dn/dt data is equally good with Fuchs and Wolf's and author's formulæ. In the infra-red, both theories agree, but both give an algebraically lower value for dn/dt than the experimental value, the difference between theory and experiment becoming greater with increase of wavelength. Precisely the same type of discrepancy is found with sylvine also. Its significance will be discussed in a later section.

(*b*) *Sylvine.*—Fuchs and Wolf's formula (Eq. 13) was used for the calculation of the thermo-optic properties. It is found that good agreement with experiment is obtained with the following values of χ for the ultra-violet frequencies:

$$\chi\,(529\text{ Å}) = 0,\ \chi\,(1083\text{ Å}) = -13\times 10^{-6},\ \chi\,(1621\text{ Å}) = 90\times 10^{-6} \qquad (18)$$

As with rocksalt, a trial value of $\chi\,(70{\cdot}7\,\mu) = 150\times 10^{-6}$ was used for the infra-red frequency. This did not affect any of the dn/dt values except the one at 21 μ. In Table V, the calculated and experimental values of dn/dt are given. It will be seen that just as with rocksalt, the agreement between the two is good upto about 2 μ after which it progressively worsens. The values of dn/dt in the ultra-violet calculated from theory are also included in the Table. They show variations similar to those exhibited by rocksalt. It can be confidently predicted that the trend of the dn/dt-wavelength curve would be verified, and that dn/dt would be found to reverse sign and become positive near about 2000 Å.U.

TABLE V

Wavelength in microns	$dn/dt \times 10^6$	
	From theory	From experiment
0·200	+ 29·8	..
0·215	0·0	..
0·257	− 24·7	..
0·340	− 32·3	..
0·434	− 35·7	− 35·57
0·589	− 36·1	− 36·41
1·4	− 36·6	− 36·46
5·0	− 36·5	− 35·72
8·85	− 35·7	− 31·14
21·0	− 25·8	− 6·3

4. Application of the Theory to Potassium Iodide

Unlike for rocksalt and sylvine, no dispersion formulæ have previously been suggested for potassium iodide, and so a formula was constructed by the author. Detailed dispersion data for potassium iodide are available

from the work of Gyulai (1927) from 0·254 to 0·615 μ and from that of Korth (1933) from 0·546 to 29 μ. The latter has also determined dn/dt for λ 5461 Å.U. between 38° and 90° C. The refractive index determinations of Gyulai and Korth are not at the same temperature, the former being at 66° and the latter at 38° C. Since dn/dt is known for only one wavelength, it is not possible to reduce both measurements to the same temperature. The difficulty has been overcome by developing two separate dispersion formulæ, one valid for the infra-red above 5 μ at 38° C. and the other valid for the ultra-violet and the visible at 66° C. The two are however related as will be clear later. From the work of Hilsch and Pohl and of Schneider and O'Bryan quoted earlier, it is known that the ultra-violet frequencies are at wavelengths 0·2190 μ, 0·1875 μ, 0·1745 μ and 0·1290 μ. In the dispersion formula for shorter wavelengths given below, the second and third ultra-violet frequencies which form a relatively close doublet have been replaced by a single frequency in the mean position 0·1805 μ. The infra-red frequency is at 102·0. In the infra-red, beyond about 5 μ the contribution to refractive index due to the ultra-violet frequencies is practically a constant and the variations in refractive index are entirely due to the infra-red frequency. Thus, from about 5 μ to 29 μ, the data of Korth (*loc. cit.*) at 38° C. can be represented by the formula

$$n^2 - 1 = C + a_R \lambda^2/(\lambda^2 - \lambda_R^2) \qquad (18)$$

with $\lambda_R = 102.0\,\mu$, $C = 1{\cdot}6499$, $a_R = 2{\cdot}530$. The agreement of this formula with experiment can be seen from Table VI. It will be noticed that the difference between the calculated and experimental values of refractive index scarcely exceeds one unit in the fourth decimal place.

TABLE VI

Wavelength in microns	Refractive index		$(n_{cal} - n_{exp}) \times 10^4$
	Calculated	Measured	
4·125	1·6266	1·6269	− 3
8·840	1·6220	1·6219	+ 1
10·02	1·6202	1·6201	+ 1
11·79	1·6171	1·6172	− 1
14	1·6128	1·6128	0
18	1·6026	1·6027	− 1
22	1·5894	1·5895	− 1
26	1·5728	1·5729	− 1
28	1·5632	1·5629	+ 3
29	1·5579	1·5571	+ 8

In the ultra-violet and visible upto $0{\cdot}615\,\mu$, for which range the data of Gyulai (*loc. cit.*) are available, the contribution to $(n^2 - 1)$ of the infra-red term has been calculated and found to be less than one unit in the fifth decimal place. The data are correct only to one unit in the third decimal place, and are given only to four decimal places. One can thus completely neglect the infra-red term in this region of the spectrum. The data are fitted well by a formula of the type

$$n^2-1 = A + \sum_{r=1}^{3} a_r \lambda^2/(\lambda^2 - \lambda_r^2) \tag{19}$$

with the three dispersion frequencies mentioned above. The numerical formula is

$$n^2 - 1 = 0{\cdot}4532 + \frac{0{\cdot}1780\,\lambda^2}{\lambda^2 - (0{\cdot}2190)^2} + \frac{0{\cdot}8027\,\lambda^2}{\lambda^2 - (0{\cdot}1805)^2} + \frac{0{\cdot}2150\,\lambda^2}{\lambda^2 - (0{\cdot}1290)^2} \tag{20}$$

The fit of the formula can be judged from Table VII, where the errors are given in units of the third decimal place. It will be seen that the error is nowhere larger than one unit, which is the limit of experimental error.

TABLE VII

Wavelength in microns	Refractive Index		$(n_{cal} - n_{exp}) \times 10^3$
	Calculated	Measured	
0·2536	2·0172	2·0169	+ 0·3
0·26520	1·9454	1·9452	+ 0·2
0·28035	1·8848	1·8847	+ 0·1
0·29673	1·8391	1·8393	− 0·2
0·31318	1·8060	1·8070	− 1·0
0·33415	1·7749	1·7754	− 0·5
0·36502	1·7431	1·7434	− 0·3
0·40466	1·7162	1·7169	− 0·7
0·43583	1·7013	1·7018	− 0·5
0·49160	1·6831	1·6832	− 0·1
0·54607	1·6713	1·6711	+ 0·2
0·57907	1·6659	1·6656	+ 0·3

From Eq. (20) the value of $(n^2 - 1)$ for very large wavelengths, which we may denote by $(n_\infty'^2 - 1)$ comes out to be 1.6479 at 66° C. It is obvious that this must correspond to C of Eq. (18) which holds for 38° C. It is not surprising that the value of $(n_\infty'^2 - 1)$, *i.e.*, the portion of $(n_\infty^2 - 1)$ due to the ultra-violet frequencies alone should be larger at 38° than at 66° C. This is because dn/dt at 5461 Å.U. is negative, and since the infra-red contribution at this wavelength is negligible, dn_∞'/dt would also be expected to negative.

We shall now apply these formulæ for calculating the thermo-optic properties. Since at 5461 Å.U. the contribution due to the infra-red frequency is negligibly small, Eq. (19) can be used. Differentiating this and using the usual notation.

$$2n\, dn/dt = -\gamma (n^2 - 1) + \frac{dA}{dt} + \sum_1^3 \frac{2a_r \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \cdot \chi_r \qquad (21)$$

Substituting the values $dn/dt = 5 \times 10^{-5}$ and $\gamma = 1 \cdot 27 \times 10^{-4}$ (from Fizeau's data quoted in Liebisch, 1891) and also the values of a_r and λ_r, one gets

$$80 \cdot 6 \times 10^{-6} = 0 \cdot 5114\, \chi_1 + 1 \cdot 970\, \chi_2 + 0 \cdot 4821\, \chi_3 + dA/dt \qquad (22)$$

It is clear that the term $-\gamma (n^2 - 1)$ is the part due to density changes, so that $80 \cdot 6 \times 10^{-6}$ is the total contribution due to changes of frequency. Now, from the measurements of Fesefeldt quoted above, χ_1 the proportional change of the ultra-violet frequency at 2190 Å.U. comes out to be 163×10^{-6}, so that the term $0 \cdot 5114\, \chi_1 = 82 \cdot 4 \times 10^{-6}$. It will be noticed that this is of the same order as the total contribution due to frequency changes, but slightly larger. Since further data on dn/dt or on the other χ's are not available, one is not in a position to make a more exact verification of our theory. Fesefeldt has actually measured the shift of the longer wavelength component of the doublet at 1805 Å.U.; but its peak intensity also diminishes, so that one cannot say how the mean position of the doublet changes. However, by analogy with rocksalt and sylvine, the result obtained here is reasonable. In these cases, it was found that the contribution due to the shift of nearest ultra-violet frequency formed the bulk of the contribution due to frequency shifts towards dn/dt. It was in fact slightly larger than the total contribution, the resultant of those from the rest being slightly negative. The above figures for potassium iodide, taking the actually observed value of χ_1, exhibit exactly the same behaviour, thus providing a direct experimental verification of our theory.

5. Discussion of the Results

The most interesting result that emerges from the present studies is with regard to the values of χ for the different ultra-violet absorption frequencies. In all the three cases studied, a certain amount of similarity has been observed. The nearest absorption has a large positive χ which is of the order of 100×10^{-6}, and the contribution of all the others taken together is slightly negative. In rocksalt the second absorption has a relatively small positive χ (25×10^{-6}), while the next one to this has a negative value (-30×10^{-6}). In other words, while the first two move towards longer wavelengths, the third shifts towards shorter wavelengths. We have not

encountered negative values for χ in the previous cases studied. However, they seem to be the rule for the deeper levels in the alkali halides. It is not possible to conjecture a definite reason for this. A probable explanation may be suggested on the following lines. It is generally supposed that the characteristic absorptions at longer wavelengths are due to the negative ions and those at shorter wavelengths are due to the positive ions. In fact, attempts have been made to interpret the actual transitions corresponding to those at longer wavelengths on these lines (see Mott and Gurney, 1940). Also, it is a fairly well established fact that the ionic character of these salts increases with rise of temperature. For example, Cauchy's relations between the elastic constants are not true for rocksalt at low temperatures, but become more and more nearly valid as the temperature is raised (Seitz, 1944), which is attributed to the increasing accuracy with which one may consider the binding in the crystal to be due to purely ionic central forces. An increase in ionic character means that the charges on the individual ions increase with temperature. The effect of this on the positive ions will be to decrease the screening effect of the outer electrons, and thus in effect to increase the nuclear charge. Thus, the frequencies would be increased. The reverse is to be expected for the negative ions. Besides, there is a general expansion of the lattice with increase of temperature which would tend to decrease the energies of all the levels. As a result one would expect the energy levels of the negative ion to be appreciably diminished and those of the positive ions to be either diminished to a much smaller extent, or to be increased, the alternative being determined by the particular conditions.

Another interesting fact is with regard to the values of dn/dt in the infra-red. In Section 3 it was mentioned that the calculated values were algebraically less than the experimental values and that the difference between the two progressively increased for longer wavelengths in the infra-red. This is the case both for rocksalt and sylvine. Such a situation would arise, if the infra-red frequency varied much more rapidly with temperature than was assumed to be the case. This explanation is not upheld by a closer scrutiny of the facts. We know from Eq. (14) that the contribution to $2n\ dn/dt$ due to the variation of the infra-red frequency is equal to $2a_R\chi_R\lambda^4/(\lambda^2 - \lambda^2_R)^2$, where λ_R is the wavelength of this frequency. If we attribute the whole discrepancy to the cause mentioned just now, χ_R will have to be of the order of 2 to 5×10^{-3}, which is altogether too large. It means that the frequency would be halved by a rise in temperature of a few hundred degrees, which is certainly not true. Further, the discrepancy between the calculated and observed values is not proportional to

$\lambda^4/(\lambda^2 - \lambda_R^2)^2$, but roughly to $\lambda^2/(\lambda^2 - \lambda_R^2)$. The coefficient of proportionality with the latter type of variation is roughly equal to $1{\cdot}6 \times 10^{-3}$ with rocksalt and $0{\cdot}54 \times 10^{-3}$ with sylvine. A variation of this type means that the quantity a_R in the numerator of the infra-red dispersion term diminishes at these rates. Dividing by a_R, one obtains the proportional rates of change of a_R in the two cases to be roughly $-4{\cdot}5 \times 10^{-4}$ and $-2{\cdot}0 \times 10^{-4}$.

Now, a_R is proportional to $N_R f_R$ where N_R is the number of dispersion centres and f_R the transition probability. We have already allowed for the decrease due to change in the number arising from thermal expansion. Since we find a further diminution, it must be due to a decrease of f_R, the transition probability. Now,

$$\frac{1}{a_R}\frac{da_R}{dt} = \frac{1}{N_R}\frac{dN_R}{dt} + \frac{1}{f_R}\frac{df_R}{dt} \tag{23}$$

$$= -\gamma - \eta, \text{ (say)} \tag{24}$$

where γ is the coefficient of cubical expansion and η the proportional change of the transition probability. Previously, we had always put $da_R/dt = -\gamma a_R$, assuming the transition probability not to alter with temperature (*cf.* Ramachandran, 1947 *a*). The case of the alkali halides shows that one has also to take the latter effect into consideration. In fact, from the rough calculations given above, η is of the same order as γ, being four times as much in rocksalt and double in sylvine.

The above discussion is, of course, based on the supposition that the experimental results are correct. One should not overlook the possibility of these being wrong. This is particularly so since the data both for rocksalt and sylvine in the infra-red are due to the same worker (Liebreich, *loc. cit.*) and some systematic errors could have crept into the measurements. It would be useful to check Liebreich's data for some wavelengths in the infra-red.

The possibility of experimental errors should not be disposed of lightly because it is not at all clear on theoretical grounds as to why the transition probability should diminish with increase of temperature. In fact, one would suppose that the reverse would be the case, considering the behaviour of its classical analogue, the oscillating dipole moment. On account of the larger lattice spacing and also because of the increasing ionic character of the crystal, one would expect the dipole moment to increase with temperature. Here again, experiment must decide the issue. For quartz it has been found that the peak absorption diminishes with increasing temperatures (Parlin, 1929), but the band also becomes broader. It

is not known what happens to the integrated value of the absorption coefficient. It may be mentioned that a test of our theory in this direction is not difficult; for the diminution of the total strength of the term ($a_R = N_R f_R$) due to thermal expansion alone will be only a small fraction (1/5 in rocksalt and 1/3 in sylvine) of what it would be if the transition probability also changed to the extent required by the dn/dt data.

In conclusion, I wish to sincerely thank Prof. Sir C. V. Raman for the kind and encouraging interest he took in this investigation.

Summary

A direct verification of the general theory of thermo-optic behaviour has been obtained by applying it to the alkali halides. Rocksalt, sylvine and potassium iodide have been considered in detail. For this purpose, new dispersion formulæ embodying observed absorption frequencies have been developed for NaCl and KI. With KI, it is found that the proportionate variation χ [$= -d(\log \nu)/dt$] of the first ultra-violet frequency at 2190 Å.U. measured by Fesefeldt agrees with what is calculated from the dn/dt data, thus verifying the fundamental basis of the author's theory. The theory successfully explains the whole course of the variation of dn/dt with wavelength in the case of rocksalt, and in particular the positive values of dn/dt near about 2000 Å.U. and its reversal in sign with increase of wavelength. The first three ultra-violet frequencies have χ's of the order of $+100\times10^{-6}$, $+25\times10^{-6}$ and -30×10^{-6} respectively, the last one near 500 Å.U. not varying with temperature. With sylvine, dn/dt measurements in the visible and near infra-red are satisfactorily explained with similar values of χ as in rocksalt. The paper also contains a general review of the dispersion data for the alkali halides. It is shown that a dispersion formula of the Drude form is more appropriate for these salts than one of the Lorentz-Lorenz form.

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THERMO-OPTIC BEHAVIOUR OF SOLIDS

VI. Optical Glasses

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1. Introduction

The thermal changes of refractive index of glasses have been studied by various workers, for a knowledge of these changes is of importance in the design of optical instruments. Temperature coefficients of the absolute index were determined by Pulfrich (1892) for a number of optical glasses of different compositions in the temperature range from room temperature upto 100° C. Reed (1898) extended Pulfrich's measurements up to 430° C. Coefficients of relative index with respect to air have been determined by Hastings (1878) and Gifford (1915, 1922) for a number of optical glasses. Peters (1926) studied both the thermal expansion and the temperature-variation of refractive indices of nine glasses up to their softening temperatures using the Fizeau interference method.* A number of very interesting facts have emerged from these investigations.

It is found that most of the silicate and borosilicate glasses, in general, exhibit an increase in refractive index with rise of temperature, the rate of change of refractive index with temperature, dn/dt, being of the order of 10^{-6}. A few crowns such as fluor-crown or phosphate crown exhibit a negative value for dn/dt. Roughly, flint glasses have values of dn/dt varying from nearly 0 for light flints containing barium to nearly 15×10^{-6} for heavy lead flints. Silicate and borosilicate crowns of low refractive index exhibit very little change of refractive index with temperature, dn/dt lying between -1 and $+3\times 10^{-6}$. However, a specimen of fluor-crown has been found to have dn/dt equal to -3×10^{-6} (Gifford, *loc. cit.*) while two phosphate crowns have values -3 and -2×10^{-6} (Pulfrich *loc. cit.*). As mentioned in Part II of these series, pure silica has an abnormally large dn/dt of $+10\times 10^{-6}$, and pyrex has a value of $+5\times 10^{-6}$, although both of these have low refractive indices. It is found that in all glasses, irrespective of whether they exhibit a positive or negative dn/dt, the dispersion $(n_C - n_F)$ always increases with rise of temperature.

* The statement made in Part I of this series that the interference method had not been used previously for determining dn/dt is not correct.

At higher temperatures, dn/dt of a glass generally increases (if originally negative, it becomes positive with rise of temperature) upto the annealing temperature. Then it rapidly diminishes and becomes negative; at the same time, the thermal expansion coefficient increases abnormally. After the softening temperature dn/dt once again attains a positive value, sometimes very large positive values. At these temperatures, the coefficient of thermal expansion is negative. All these will be clear from Fig. 1 reproduced from the paper by Peters referred to above. Here the three

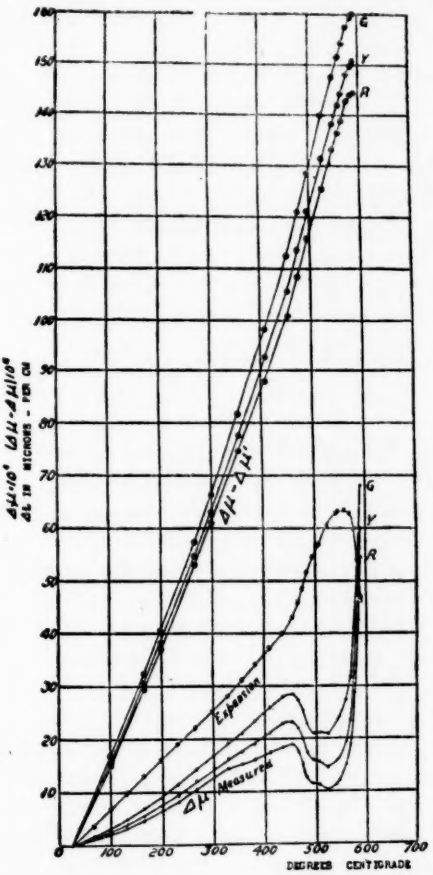

FIG. 1. Curves showing the variation with temperature of $\Delta\mu$, the measured change in refractive index from room temperature, the linear expansion and $(\Delta\mu-\Delta\mu')$, where $\Delta\mu'$ is the change in refractive index to be expected on the basis of Gladstone and Dale's law for a typical flint glass. G, Y, R stand for the helium lines of wavelengths 5017, 5877 and 6680 Å.U.

curves represent respectively $\Delta\mu$ the measured change in refractive index from room temperature, Δl the linear expansion and a third quantity $(\Delta\mu - \Delta\mu')$ in which $\Delta\mu'$ is the change in refractive index to be expected on the basis that Gladstone and Dale's law is obeyed, *viz.*, that $(n-1)/\rho$ is a constant.

It will be noticed that $\Delta\mu$ is not equal to $\Delta\mu'$, which shows that change of density alone cannot explain the variation of refractive index with temperature. This has been found to be universally the case (Pulfrich, 1892, Peters, 1926), both for glasses whose refractive index increases with temperature as well as those for which it decreases. In all cases, $(\Delta\mu - \Delta\mu')$ is positive, so that another factor is also responsible for the change of refractive index with temperature, which always produces an increase. Various suggestions have been made as regards this second factor. Pulfrich (*loc. cit.*) considered it to be the increase in intensity of the ultra-violet absorption bands and their shift towards longer wavelengths, which according to him, is evidenced by the increasing absorption towards longer wavelengths. Peters (1926) remarked that the increase in index is caused by augmented absorption, or more probably that both are produced by the same or similar causes. Tilton (1935) opined that the effect is due to the increasing capacity for absorbing radiation of longer wavelength which in effect " shifts " the absorption bands to longer wavelengths.

It is clear that all these suggestions are only of a general and qualitative nature and unless they are made more precise and definite, it is not possible to develop a quantitative theory on their basis. Now the contribution to refractive index due to a dispersion frequency is determined by two factors, *viz.*, its oscillator-strength (transition probability) and its position (value of its frequency or wavelength). The effects of a change in one or the other of these quantities on the refractive index are quite different. A variation in the transition probability would only affect the refractive index in a manner similar to that due to a change in density, *i.e.*, both the refractive index and dispersion for any wavelength would be altered in the same proportion, the effect being of opposite signs according as the dispersion frequency is in the ultra-violet or in the infra-red. On the other hand, a variation in frequency would produce much larger changes in the refractive index and dispersion for wavelengths close to the dispersion frequency than for those farther away. Besides, the changes would be of the same sign irrespective of the position of the dispersion frequency. The earlier workers do not appear to have appreciated these differences between the two types of changes that might occur to the dispersion frequencies. Pulfrich's ideas are equivalent

to assuming that both types of changes occur. Unless one has *a priori* some idea of the magnitudes of the changes, it is very difficult to develop a quantitative theory on their basis and carry out calculations for any particular case.

In the general theory of thermo-optic behaviour developed by the author (Ramachandran, 1947 *a*), it is assumed that the oscillator-strengths of the ultra-violet frequencies do not alter with temperature, and this enables one to formulate a quantitative theory for the variation of refractive index with temperature. Perhaps the best justification for the assumption lies in the success of the theory in explaining the values of dn/dt of various crystals and vitreous silica, both over a range of wavelengths and over a range of temperatures (Ramachandran, 1947 *b, c, d, e*). A theoretical justification can also be given by considering the theory of an analogous phenomenon, which is discussed in Appendix I. In this paper, it is proposed to apply the theory to the case of glasses in general. We shall follow the mathematical procedure adopted in the earlier papers and also use the same symbols and terminology.

2. Method of Calculating dn/dt

It will be clear from what has been said above that a knowledge of the dispersion frequencies of the glass is necessary for investigating its thermo-optic behaviour. In other words, one should have a dispersion formula for the refractive index of the substance for calculating dn/dt. Fortunately such a dispersion formula has been provided for us by the investigations of Huggins and co-workers (1940, 1942) in which they have developed formulæ for calculating the refractive indices and dispersion of a glass purely from a knowledge of its chemical composition. Subject to certain minor variations, their formulæ are based on the idea that each component oxide in the glass has a characteristic dispersion frequency of its own and that its contribution to the refractine index is proportional to its concentration. The numerical constants of these formulæ have been computed and given for a large number of oxides. In this paper, we shall make use of the dispersion formulæ of these workers, and proceed to calculate dn/dt on their basis.

For a proper appreciation of the present paper, it is necessary to briefly summarise the results of Huggins and coworkers. They have represented the dispersion of glasses by the formula

$$n-1=\sum_{M}\frac{A_M}{g_M-1/\lambda^2}-k\,A_M\,\lambda^2 \qquad (1)$$

where

$$g_M = 1/\lambda_M^2, \tag{2}$$

λ_M being the characteristic frequency corresponding to the component oxide $M_m O_n$; A_M is a quantity given by the expression

$$A_M = d_M N_M/V_0 \tag{3}$$

d_M being a characteristic constant for each oxide and N_M/V_0 is a factor depending on its percentage composition; k is a factor which expresses the ratio of the strength of the infra-red term to that of the ultra-violet term. Since the infra-red dispersion frequency is at wavelengths larger than 8μ, its contribution to refractive index in the visible is given by $-kA_M\lambda^2$. k is found to have the value 48×10^{-6} for all the oxides within the limits of experimental error. N_M and V_0 are given by the following relations:

$$V_0 = 1/\rho\ \Sigma\, n_M f_M/W_M \tag{4}$$

$$N_M = (m_M f_M/W_M)/\Sigma\, n_M f_M/W_M, \tag{5}$$

where n_M, m_M are the quantities n, m associated with the oxide M_mO_n, f_M is the weight fraction and W_M the molecular weight of the oxide and ρ is the density. Although the formulæ are so involved, it will be clear that the optical effects of each component oxide is characterised only by two constants, one d_M determining its optical strength and the other g_M being the inverse square of its characteristic frequency.

The formulæ are however capable of simplification. One notes that $N_M/V_0 = \rho m_M f_M/W_M$, so that if one writes $m_M d_M/W_M = c_M$, then Eq. (1) becomes

$$\frac{n-1}{\rho} = \sum_M f_M \left[\frac{c_M}{g_M - 1/\lambda^2} - k\, c_M\, \lambda^2\right]. \tag{6}$$

In this formula also, each oxide has two constants, *viz.*, c_M and g_M, and the contribution of each oxide to $(n-1)/\rho$ is given by the quantity within the square brackets multiplied by f_M, its weight fraction, which is simply the percentage composition divided by 100. This form of the dispersion formulæ considerably simplifies the numerical calculation and is used hereafter.

A few other finer points considered by Huggins and coworkers may be mentioned here as they are needed later. For lead, calcium and barium, it is found that two ultra-violet frequencies are necessary, of which the strength of the second one varies as N^2_{Pb} in the case of lead and as N_{Ca} and N_{Ba} in the other two cases. In this paper, this finer point has to be considered only for PbO. In the other two cases, the simpler formula with one

ultra-violet frequency sufficed. For PbO

$$\frac{n-1}{\rho} = f_{Pb}\left[\frac{c_{Pb}^{0}}{g_{Pb}^{0} - 1/\lambda^2} + \frac{c_{Pb}'' N_{Pb}^{2}}{g_{Pb}'' - 1/\lambda^2} - k\, c_{Pb}^{0}\, \lambda^2\right] \quad (7)$$

The wavelengths of the two dispersions frequencies, *viz.*, λ_{Pb}^{0} and λ_{Pb}'' are 1498 A.U. and 2949 A.U. In the case of boron trioxide, it is necessary to distinguish between tetrahedrally co-ordinated and triangularly co-ordinated boron, which many be denoted by B′ and B″. The separate N's of B′ and B″ are calculated from the following equations (Huggins, 1940):

if $$N_{Si} + N_B < 0.50,\ N_{B'} = N_B,\ N_{B''} = 0; \quad (8)$$

if $$N_{Si} + N_B > 0.50,$$

$$\left.\begin{aligned} N_{B'} &= 2 - 4N_{Si} - 3N_B \\ N_{B''} &= 4N_{Si} + 4N_B - 2. \end{aligned}\right\} \quad (9)$$

The two types of boron, B′ and B″ have different dispersion frequencies, that of the former having a wave length of 742 A.U. and of the latter 898 A.U. As will be seen later, the rate of variation of the former with temperature is much smaller than that of the latter.

Proceeding now to the consideration of dn/dt, we may take Eq. (6) to represent the refractive indices of glasses. Differentiating this equation and assuming that the transition probability does not vary with temperature, so that $dc_M/dt = -\gamma c_M$, one obtains

$$\frac{dn}{dt} = -\gamma(n-1) + \rho \sum_{M} f_M \cdot \frac{2c_M g_M}{(g_M - 1/\lambda^2)^2} \cdot \chi_M, \quad (10)$$

where γ is the coefficient of cubical expansion and χ_M is the proportionate variation of the dispersion wavelength λ_M, *i.e.*,

$$\chi_M = (1/\lambda_M)(d\lambda_M/dt). \quad (11)$$

In this formula, the contribution to dn/dt due to the variation of the infrared frequency with temperature has been neglected, being very small [*cf.*, the case of pure silica glass discussed in Part II (Ramachandran, 1947 *b*)]. The coefficient of cubical expansion, γ, of the glass being known, the only unknown quantities in the right hand side of Eq. (10) are the χ_M's. If one could obtain these, then it is possible to theoretically calculate the variation with temperature of the refractive index of a glass of known composition.

The ideal method of determining the χ's would be to use dn/dt data of pure oxides in the glassy state, if available, or at least of glasses made up of 2 or 3 components. Unfortunately such data are not available, with

the one exception of pure silica glass. The χ's were therefore calculated as follows. For pure silica glass, it is known (Tilton, 1929) that dn/dt for 5893 A.U. is 9.9×10^{-6}, from which χ_{Si} was calculated to be 11.27×10^{-6}. For lead, the χ's were deduced from Pulfrich's data for the glass S. 57 containing 82% Pb O and 18% SiO_2. The others were determined by considering glasses containing a large percentage of each component. The χ_M's are all tabulated in Table I together with the corresponding c_M, d_M and g_M of Eqs. (1) and (6), these being based on the calculation of Huggins, Sun and Davis (1942).

TABLE I

M	$10^{-8}d_M$	$10^{-8}c_M$	$10^{-8}g_M$	$10^6\chi_M$
Na ..	463·655	14·96	79·844	20
K ..	900·965	19·13	97·202	20
Ca ..	1228	21·90	99·7	15
Ba ..	2136	13·92	109	16
Zn ..	868·20	10·67	73·96	17
Pb' ..	1220·1	5·466	45·81	16
Pb'' ..	196	0·878	11·5	68·5
B' ..	1413·49	40·59	190·75	4
B'' ..	1067·18	30·65	123·90	11
Al ..	1200·0	23·54	118·5	16
Si ..	1790·480	29·81	145·685	11·27

The results of the theory can be compared with experiment in the following way. It will be noticed that the contribution to dn/dt due to frequency changes alone, which we may denote by $(dn/dt)_\lambda$, is equal to $dn/dt+\gamma(n-1)$. Theoretically also this quantity can be computed from the sum given in Eq. (10). Consequently, this is the quantity whose theoretical value is compared with experiment to judge the validity of our theory. In calculating $(dn/dt)_\lambda$ it is necessary to know ρ, the density of the glass in addition to the other quantities f_M, c_M, g_M and χ_M. Actually, although the percentage compositions of the glasses studied are known, their densities are not available. This difficulty has been overcome as follows. The refractive index n_D is computed from (6) for the D line but for the factor ρ, and comparing it with the measured value, the density is obtained. An additional check is available by verifying that the same value of ρ gives the partial dispersions (n_F-n_D) and (n_D-n_C) correctly. In Table II the values of $(dn/dt)_\lambda$ for the D line with Pulfrich's glasses and for the helium 'd' line with Peters' glasses calculated from the above χ's are given along with the experimental data. The compositions of the glasses are given in Table III. For all the glasses, As_2O_3 has been neglected in the calculations. The computations have been carried out only for the glasses studied by Pulfrich

Table II

Glass	$(dn/dt) \times 10^5$		Glass	$(dn/dt) \times 10^5$	
	Calc.	Expt.		Calc.	Expt.
S 57	4·158	4·159	0627	1·286	1·362
0 165	2·568	2·593			
0 544	1·832	1·730	BS 103	1·368	1·50
0 154	1·662	1·613	BS 87	1·504	1·50
0 658	1·210	1·156	BS 94	1·320	1·31
0 527	1·596	1·556	BS 33	1·632	1·69
0 211	1·526	1·390	BS 110	1·868	2·00
0 1022	1·398	1·376	BS 145	1·466	1·50
			Pyrex	1·058	1·00
S 205	0·974	0·953	Silica	1·059	1·059

Table III

Glass	Si	Ca	Na	K	As	Al	Zn	B	Ba	Pb
S 57	18	..	..	..	..	..	..	..	..	82
0 165	28·4	..	..	2·5	0·1	..	..	..	..	69
0 544	45·8	..	0·5	8·0	0·4	..	..	..	..	45·2
0 154	54·3	..	3·0	8·0	0·2	..	..	1·5	..	33·0
0 658	32·8	..	1·0	3·0	..	7·0	..	31·0	..	25·0
0 527	51·7	..	1·5	9·5	..	..	7·0	..	20·0	10·0
0 211	48·1	..	1·0	7·5	..	..	10·3	4·5	29·0	..
0 1022	65·4	..	5·0	15·0	0·4	..	2·0	2·5	9·6	..
S 205	..	..	8·0	..	..	18·0	..	69·1	4·7	..
0 627	68·2	..	10·0	9·5	0·2	..	2·0	10·0	..	..
BS 103	67·0	..	12·0	5·0	0·4	..	1·5	3·5	10·6	..
BS 87	47·6	..	2·0	6·0	1·3	..	9·9	4·0	29·2	..
BS 94	66·5	..	9·8	5·9	0·2	..	2·0	7·8	7·8	..
BS 33	54·0	2·0	1·0	6·0	0·3	..	..	..	..	36·7
BS 110	44·3	3·0	3·5	5·0	0·2	..	..	..	..	44·0
BS 145	58·8	..	1·7	8·3	..	..	2·5	1·7	14·3	12·7
Pyrex	80·5	0·3	4·4	0·2	0·7	2·0	..	11·8	..	..
Silica	100·0	..	..	..	..	..	..	..	..	..

(1892) and Peters (1926). In the former case, γ has also been measured by Pulfrich so that $(dn/dt)_\lambda$ could be calculated. In the latter case, curves of $(\Delta n - \Delta n')$, the component of the variation of refractive index due to change of frequency alone, which is equal to $\Delta n + \Delta V(n-1)$, for various temperatures are given by Peters as graphs, so that $(dn/dt)_\lambda$ could be obtained from the curves. Unfortunately Reed (1898) has not measured the thermal expansion of his glasses, so that his results could not be made use of.

It will be noticed from Table II that the values of $(dn/dt)_\lambda$ given by theory agree reasonably well with the measured values considering the

complexity of composition of most of the glasses. It should be emphasised that the χ's in Table I are not very accurate, since they have been deduced from measurements on multi-component glasses. It would appear that, if one could obtain measurements of dn/dt with glasses having only 2 or 3 componehts in various proportions, then the χ_M's can be determined more accurately, and a prediction of dn/dt for a glass of any composition can be made with greater accuracy.

3. Dispersion of dn/dt.

Pulfrich has measured dn/dt of his glasses for four wavelengths in the visible, *viz.*, C, D, F and G′ lines. One can therefore find out how far the

Table IV

Glass		$(dn/dt)_\lambda \cdot 10^5$				$(dn/dt)_\lambda \times 10^5$
		C	D	F	G′	G′ − C
S 57	Exp.	3·874	4·157	4·897	5·708	1·834
	Th.	3·908	4·158	4·839	5·710	1·802
O 165	Exp.	2·500	2·593	2·917	3·218	0·718
	Th.	2·460	2·568	2·822	3·112	0·652
O 544	Exp.	1·681	1·730	1·865	2·003	0·321
	Th.	1·802	1·836	1·920	1·998	0·196
O 154	Exp.	1·568	1·613	1·708	1·800	0·232
	Th.	1·636	1·662	1·722	1·776	0·140
O 658	Exp.	1·118	1·156	1·224	1·285	0·167
	Th.	1·186	1·210	1·246	1·274	0·088
O 527	Exp.	1·541	1·556	1·643	1·718	0·177
	Th.	1·580	1·596	1·640	1·678	0·098
O 211	Exp.	1·364	1·390	1·469	1·521	0·157
	Th.	1·512	1·526	1·566	1·596	0·084
O 1022	Exp.	1·345	1·376	1·438	1·502	0·157
	Th.	1·384	1·398	1·428	1·458	0·074
S 205	Exp.	0·956	0·953	1·006	1·045	0·089
	Th.	0·966	0·974	1·000	1·014	0·048
O 627	Exp.	1·340	1·362	1·419	1·464	0·124
	Th.	1·274	1·286	1·314	1·342	0·068

theory given above is able to explain the variations of dn/dt with wavelength. $(dn/dt)_\lambda$ was calculated from theory for these wavelengths using the values of c_M, g_M and χ_M given in Table I. They are shown in Table IV together with the experimental values as given by Pulfrich's data for the optical glasses. It will be noticed from the table that the agreement between theory and experiment is not as good as could be expected. In fact, the calculated change in $(dn/dt)_\lambda$ from the C to G′ line is, in general, only about half of what is observed. This happens even for pure silica. The explanation of the discrepancy is not far to seek; it lies in the fact that the form of the dispersion formula used is not a sufficiently close approximation to truth for it to give the dispersion of dn/dt accurately. We shall illustrate this with special reference to silica glass. In Part II of this series the dispersion of vitreous silica was represented by a formula of the type

$$n^2 - 1 = C + \frac{A\lambda^2\lambda^2_{Si}}{\lambda^2 - \lambda^2_{Si}} - K\lambda^2. \qquad (12)$$

Following the theory of Huggins and co-workers, which we have used in this paper, the dispersion formula for pure silica glass will be of the form:

$$n - 1 = \frac{A_{Si}}{\left(\frac{1}{\lambda_{Si}^2} - \frac{1}{\lambda^2}\right)} - K\lambda^2 = \frac{A_{Si}\lambda^2\lambda_{Si}^2}{\lambda^2 - \lambda^2_{Si}} - K\lambda^2. \qquad (13)$$

The appearance of $(n-1)$ in formula (13) instead of (n^2-1) would not lead to a serious error, for the formula is expected to hold only for the visible region of the spectrum, in which $(n+1)$ is sensibly constant. The important difference is that while (12) has two terms to represent the contribution of the ultra-violet frequencies, (13) has only one. In Eq. (12), the constant term C arises from the presence of a remote ultra-violet frequency. Consequently, λ_{Si} in Eq. (12) is much nearer to the visible than in Eq. (13), the two values being actually 1070 A.U. and 828 A.U. We have shown in Part II that Eq. (10) represents dn/dt correctly right from 2000 A.U. to 7000 A.U. Because of the restricted range of its application (*viz.*, from 4000 to 7000 A.U.), (13) is able to give the same refractive indices and dispersion as (12). These involve only terms like $1/(\lambda^2 - \lambda_{Si}^2)$ and $1/(\lambda^2 - \lambda_{Si}^2)^2$ respectively, and for the same reason, Eq. (13) also gives $(dn/dt)_\lambda$ fairly accurately, for this also involves only terms like $1/(\lambda^2 - \lambda_{Si}^2)^2$. But the dispersion of dn/dt involves terms like $1/(\lambda^2 - \lambda_{Si}^2)^3$, so that one should not be surprised if Eq. (13) does not agree well with experiment with regard to this aspect. It is also possible to deduce in which direction theory would deviate from experiment. As mentioned above, Eqs. (12) and (13) agree in giving the same

refractive index and dispersion, which means that variations occurring in terms like $1/(\lambda^2 - \lambda_{Si}^2)$ in the two formulæ are the same. $(dn/dt)_\lambda$ however varies as $1/(\lambda^2 - \lambda_{Si}^2)^2$, and since λ_{Si} in (13) is smaller than that in (12), the theoretically calculated dispersion of (dn/dt) would be lower than what is actually observed, as shown by Table IV.

The above considerations discussed with special reference to SiO_2 should also obviously hold for the other oxide components. This shows the way towards improving the dispersion formula so as to give the dispersion of dn/dt also fairly accurately. What is necessary is that, instead of using only one frequency in the ultra-violet, another remote dispersion frequency should also be employed, whose contribution in the visible region would be a constant. The improved dispersion formula would take up the form

$$\frac{n-1}{\rho} = \sum_M f_M \left[b_M + \frac{c_M}{g_M - 1/\lambda^2} - k_M \lambda^2 \right], \tag{14}$$

which differs from (6) in containing only an additional constant for each component. To simplify matters, one may put $k_M = k' c_M$, as done by Huggins and coworkers, so that it is necessary to determine only three constants for each oxide component, *viz.*, b_M, c_M, and g_M. A preliminary attempt has been made to obtain the values of these constants for just a few oxides. It is found that by applying Eq. (14), the dispersion of $(dn/dt)_\lambda$ comes out correctly.

4. Application of the New Dispersion Formula

In obtaining an expression for dn/dt we shall make use of the result found in the previous parts of this series that the significant part of the contribution due to change of frequency arises only from the nearest ultra-violet frequency. Thus, the remote ultra-violet frequency is taken not to alter with temperature. Hence, the change of b_M with temperature is only due to change in density, so that $db_M/dt = -\gamma b_M$. Thus, one obtains from (14),

$$dn/dt = -\gamma (n-1) + \rho \sum_M f_M \cdot \frac{2 c_M g_M}{(g_M - 1/\lambda^2)^2} \cdot \chi_M, \tag{15}$$

which is identical with (10) except that the constants c_M, g_M and χ_M are now different.

The determination of the constants in (14) was done in the following manner. If we designate $(n-1)/\rho$ for any wavelength by 'r' the specific refraction, then Eq. (14) requires that

$$r = \sum_M f_M r_M, \tag{16}$$

where r_M is the specific refraction of the particular oxide. Knowing the refractive indices of two and three component glasses of varying composition, r_M for the D line could be determined as has been done by Young and Finn (1940). In this work, the author has assumed the values of r_M for the D line given by these workers, as also the values of r_M (F— C). For SiO_2, Na_2O, K_2O, CaO and PbO the author worked out the values of r_M (D— C) from the values of $(n_D - n_C)$ given for various three component glasses in Morey's book (1935) on "Properties of Glass", Ch. XVI. Since the calculations were intended to be only of an exploratory type, elaborate least square methods were not used, but only a few data were taken to evaluate these. In Table V are given the values of r_M (D), r_M (D— C), r_M (F— D) for these oxides.

TABLE V

	$r_M(D)$	$r_M(D-C)$	$r_M(F-D)$
SiO_2	0·2082	0·00093	0·00212
Na_2O	0·1937	0·00140	0·00355
K_2O	0·2019	0·00124	0·00296
CaO	0·2270	0·00137	0·00357
PbO	0·134	0·0018	0·0048

From these, knowing the values of γ_M for three wavelengths, it is a simple matter to determine b_M, c_M and g_M. The infra-red term in (14) was neglected in these calculations. The values of these constants are shown in Table VI together with λ_M, the wavelengths of the dispersion frequencies and χ_M their proportional variation with temperature, which were calculated in the manner to be described below.

TABLE VI

	b_M	$c_M \cdot 10^{-8}$	$g_M \cdot 10^{-8}$	λ_M in A.U.	$\chi_M \cdot 10^6$
SiO_2	0·0656	12·03	87·26	1070	16·3
Na_2O	0·0795	4·669	47·69	1448	12
K_2O	0·0667	8·424	65·19	1239	10
CaO	0·1068	5·613	49·58	1420	..
PbO	0·0512	2·073	27·92	1892	30·3

It is found that for concentrations of PbO greater than 60% its contribution to the specific refraction was not proportional to f_{Pb} but increases much more rapidly. This has been sought to be taken account of by introducing an additional term proportional to N_{Pb}^2 in the theory of

Huggins and co-workers. This was not attempted in the new formula, so that they are not valid for concentrations of PbO greater than 60%.

The dn/dt calculations were carried out only for three glasses, namely O 165, O 544 and O 154 of Table III. These contain only four components SiO_2, Na_2O, K_2O and PbO, As_2O_3 which forms less than 1% being ignored. Taking the values of $(dn/dt)_\lambda$ for the D line only and using Eq. (15), the χ's in Table VI were determined so as to obtain the best fit. It will be clear that the values for Na_2O and K_2O are very approximate, since they occur only in small proportions. The principal constitutens are lead and silica. The values of $(dn/dt)_\lambda$ for the four lines C, D, F and G', calculated with the data in Table VI are shown in Table VII, along with the experimental results. It will be seen that the dispersion of $(dn/dt)_\lambda$ is given quite accurately. For O 165 the theoretical dispersion is lower. This is because it contains 69% of lead, and as mentioned above an additional term has to be taken. The discrepancy is due to the neglect of this term.

TABLE VII

Glass		$(dn/dt)_\lambda \cdot 10^5$				$(dn/dt)_\lambda \cdot 10^5$
		C	D	F	G'	G' − C
O 154	Th.	1·558	1·598	1·704	1·798	0·240
	Exp.	1·568	1·612	1·708	1·800	0·232
O 544	Th.	1·732	1·780	1·914	2·042	0·310
	Exp.	1·680	1·730	1·866	2·004	0·324
O 165	Th,	2·462	2·554	2·794	3·018	0·556
	Exp.	2·500	2·594	2·916	3·218	0·738

It will be noticed that the modification of the dispersion formula has enabled it to give the dispersion of dn/dt also correctly. It is to be noted that the calculations in the whole of this section is only of a preliminary nature. The attempt has been only to show the utility of the modified formula. The numerical values of the constants in the formula are not very accurate.

5. General Discussion of the Theoretical Results

We have seen how the theory is able to explain reasonably well the numerical data of Pulfrich and of Peters. In addition, it enables one to understand qualitatively various other phenomena mentioned in Section 1.

It will be noticed from Table I that, but for boric oxide, all the other oxides have nearly the same values of χ, lying between 10 and 20×10^{-6}. If lead is present in large amounts, then the term involving Pb'' comes in, which has a large χ of nearly 70×10^{-6}. Thus, one would find that $(dn/dt)_\lambda$ is nearly the same for all silicate glasses, which do not contain a large percentage of lead. A perusal of Table II will show that this is true and that $(dn/dt)_\lambda$ lies between 1.3 and 1.6×10^{-6} for such glasses. Consequently, the actual temperature-variation of refractive index of such glasses will depend on the thermal expansion, those having a large thermal expansion showing a small positive or negative dn/dt and *vice-versa*. If the glass contains a large percentage of PbO, then it would be expected to show a large positive dn/dt. Borates or borosilicates containing a large percentage of boric oxide would be expected to show a negative dn/dt, on account of the particularly low value of χ for B_2O_3.

On the other hand, even among silicates, if the glass has a particularly low thermal expansion, then it would exhibit a large increase of refractive index with temperature. Such is the case with pyrex, and particularly with pure vitreous silica, for which the coefficient of thermal expansion is extremely small.

In a similar manner, the variations in thermal expansion are adequate to explain the anomalous changes in dn/dt near annealing and softening temperatures, observed by Peters (*loc. cit.*) and described in section 1 of this paper. It will be noticed that although both the expansion and the change in refractive index show anomalous variations at these temperatures, the quantity $(\Delta\mu - \Delta\mu')$, which according to our theory, is the change in refractive index due to the alteration of the frequencies alone, shows a continuous variation throughout the whole range of temperatures. It increases continuously with temperature, the rate of change $(dn/dt)_\lambda$ also increasing with temperature. It is obvious from this that the changes occurring in the dispersion frequencies are to a large extent independent of all other influences except that of temperature. This is shown also by another result obtained by Peters, *viz.*, that, although the refractive index and dn/dt are to a slight extent dependent on the previous heat treatment of the glass, $(dn/dt)_\lambda$ is much less so. Consequently, it is not surprising that dn/dt shows anomalous changes at and above the annealing temperatures. Although the frequency component of dn/dt varies continuously, the density component changes anomalously, so that dn/dt as a whole suffers anomalous changes. It will be noticed that, as a result, there should be a reverse correlation between dn/dt and thermal expansion, the former decreasing while the latter increases and *vice versa*, as is actually observed to be the case.

Another interesting fact to be noticed is with respect to the values of χ at higher temperatures. It was mentioned just now that $(dn/dt)_\lambda$ increases with rise of temperature. The values for the He ' d ' line for some typical glasses studied by Peters (*loc. cit.*), as deduced by the author from his curves, are given in Table VIII. It will be seen from the table that the increase of $(dn/dt)_\lambda$ with rise of temperature is a universal phenomenon. This is possible only if all the χ's also increase with temperature. It might be noticed that this result was obtained for pure silica glass in Part II. Here one finds that, for every one of the oxide components, the proportional rate of change increases with rise of temperature. This result is of great interest for we have found it to be the case with crystals, and now it is applicable to the glassy state of solids as well. The trend of the $(dn/dt)_\lambda$ *vs* t curves show that the rates of change probably vanish at low temperatures. Further measurements on glasses at low temperatures are necessary to verify this.

TABLE VIII

Glass	$(dn/dt)_\lambda \cdot 10^6$ at °C.				
	60	150	250	350	450
B S 103 ..	15	19	20·5	21·5	24
B S 87 ..	15	17·5	18·5	20	20
B S 94 ..	13	16	17·5	18	18·5
B S 33 ..	17	19	20	21·5	25
B S 110 ..	20	22	24	26	30
B S 145 ..	15	16	18·5	19·5	21
Pyrex ..	10	14	14	14	15·5

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman for the kind and encouraging interest he took in this investigation.

SUMMARY

In this paper, the author's general theory of thermo-optic behaviour is applied to the case of optical glasses. Making use of the dispersion formulæ of Huggins and co-workers, which employs one dispersion frequency for each oxide component, formulæ are developed, which give the rate of change of the refractive index with temperature, dn/dt. Computations made on the basis of these formulæ give fairly correct values of dn/dt for a large variety of multicomponent optical glasses studied by Pulfrich and by Peters. Although the formulæ give dn/dt fairly correctly for any particular wavelength in the visible, they do not give accurate values for the dispersion of dn/dt. The discrepancy is shown to be due to the

inadequacy of using one dispersion frequency for each component in the dispersion formula. Using two frequencies, one of which is in the remote ultra-violet, and gives only a constant contribution to refractive index, new dispersion formulæ are derived and on their basis both *dn/dt* for any wavelength as well as its dispersion are correctly obtained. In addition, the theory also explains qualitatively other observations made on the thermo-optic behaviour of optical glasses, such as the anomalous variations of *dn/dt* near the annealing and softening temperatures and broadly the correlation between composition and the value of *dn/dt* of the glasses. It is inferred that the proportionate variation of the dispersion frequencies of all the components diminishes with fall of temperature, and probably vanishes at very low temperatures, as is the case with crystals like diamond.

Appendix I

The author's theory of thermo-optic behaviour makes use of the assumption that the transition probability of the ultra-violet frequencies does not vary with temperature. The assumption is not, however, unique to this theory, for exactly the same result occurs in the theory of the Faraday effect, or the rotation of the plane of polarisation of a beam of light by a substance under the influence of a magnetic field. This phenomenon has been explained on the basis of changes that occur in the ultra-violet dispersion frequencies (Schutz, 1936). Just as we have mentioned earlier with regard to temperature, three quantities can alter when the field is put on, *viz.*, the frequency ω_0, the oscillator-strength f and the density of dispersion centres N. The expression for the magnetic rotation involves the difference in the refractive indices n_- and n_+ of the two circularly polarised components, which takes the form:

$$\delta n = n_- - n_+ = -\left(\frac{\partial n}{\partial \omega_0}\,\delta\omega_0 + \frac{\partial n}{\partial f}\,\delta f + \frac{\partial n}{\partial N}\,\delta N\right).$$

On this basis, formulæ can be developed which give the magneto-optic anomaly γ, *i.e.*, the ratio of the observed rotation to what is calculated on the basis of Becquerel's formula. γ is given by (Schutz, *loc. cit.*)

$$\gamma = a + \frac{b}{2}\cdot\frac{(\omega_0^2 - \omega^2)}{\omega_0 \cdot \Delta\omega_0} + \frac{c^*}{2}\cdot\frac{(\omega_0^2 - \omega^2)}{\omega_0}\cdot\frac{h}{kT}$$

in which a, b, c^* are constants characteristic of the substance and $\Delta\omega$ is the Zeeman splitting. In this formula, the three terms on the right hand side correspond respectively to the three terms in the previous equation. It can be shown that for a diamagnetic substance the third term is zero. Also, under certain circumstances, the coefficient b in the second term can be proved to be equal to zero (Schutz, *l.c.*, p. 87). This means that the

change in the oscillator-strength is zero. Also, it is a fairly well-established fact that, for a diamagnetic, γ is a constant over the range of wavelengths in which the substance is transparent (Darwin and Watson, 1927; Schutz, *loc. cit.*, Ramaseshan, 1946, 1947). This means that the second term in the expression for γ cannot have any appreciable weight, for it is proportional to $(1/\lambda^2_0 - 1/\lambda^2)$, which varies with wavelength. From this also one may conclude that the oscillator-strength does not alter sensibly in the presence of the magnetic field.

It is not the intention of the author to suggest that the Faraday effect and the thermal variation of refractive index are closely related phenomena. But it is clear that the processes occurring in them are analogous, since both depend on the alteration of the course of the dispersion curve, which has its origin in the changes occurring in the dispersion frequencies.

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INFLUENCE OF THE APPLIED POTENTIAL ON THE *JOSHI-EFFECT*

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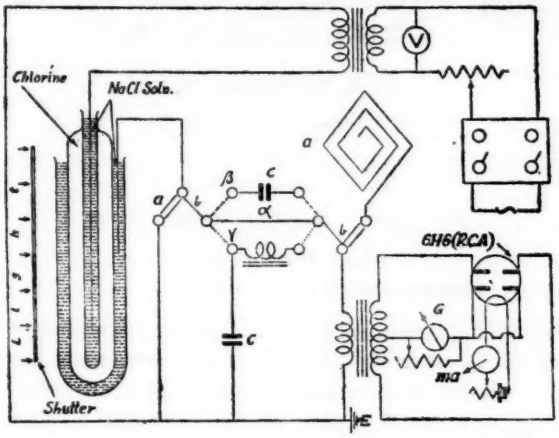
§ 1. The basic significance of the applied potential V in the production of the above effect Δi, defined as a photo-diminution of the discharge current i, is revealed by the general findings of Prof. Joshi, that Δi does not occur below V_m, the 'threshold potential' at which the gas breaks down as a dielectric[1,2]; and that $\% \Delta i$ (*vide infra*) tends to a maximum near V_m.[3] Previous studies of this effect[4,5,6] were restricted to the change (on irradiation) of the circuit current i_{LT} observed between the low tension electrode and earth. The marked complexity of the structure of the discharge current above V_m has been emphasised by Joshi[3,7,8,9]; according to him, the high frequency component of i would appear to be the chief seat of this phenomenon. It was of interest therefore, to investigate the variation with the applied potential, of the *Joshi-effect* in the high and low frequency regions constituting i the discharge current.

§ 2. Alternating potentials of 50 cycles frequency obtained from a rotary convertor and stepped up with a transformer, were applied to a Siemens' glass ozoniser, containing chlorine, purified over liquid air, at about 300 mm. pressure (see Fig. 1). The *Joshi-effect* Δi was studied as follows.

In each series, observation of current was made in dark (i_D); and under irradiation (i_L) from a 220 volt, 200 watt incandescent (glass) bulb; a double diode 6H6 (RCA) was employed as a biphase half-wave detector: In the first series, the discharge current was picked up by a moderate size frame aerial (a, in Fig. 1) kept near the chlorine tube. This i_{aerial} was admitted to the primary of a Bell transformer; its secondaries were connected separately to each plate of the diode. The cathodes were connected together to the centre of the transformer secondary through a reflection galvanometer (G) with an appropriate shunt. This part of the circuit is shown by a in Fig. 1.

Fig 1. Joshi-effect in H.F., L.F. Regions of Discharge Current



A group of three series of observations of i was next made in the LT circuit (*cf.* *b* in Fig. 1): In the first, this current from the chlorine tube (i_{LT}) was input directly to the detector. Secondly, the LF component in the i_{LT} was blocked by a condenser C of $0{\cdot}0001\mu F$ connected in series with the LT line; finally, the i_{LF} was allowed to flow in the detector circuit and the i_{HF} was by-passed to the earth through C. The circuits used in these experiments are shown in Fig. 1 by α, β and γ respectively.

A low resistance Cambridge vacuo-junction was next substituted for the diode under otherwise identical conditions of excitation, and the detector arrangement, *viz.*, *a*, α, β and γ.

The curves in Fig. 2 (*a*), (*b*), (*c*) and (*d*) show respectively the current in dark i_D and in light i_L in each of the following components: i_{aerial}, i_{LT}, i_{HF} and i_{LF} in the range 5–9 kV applied to the ozoniser. In experiments to which Fig. 3 refers the double diode was substituted by a vacuo-junction. The net *Joshi-effect* $\Delta i = i_D - i_L$ in any of the above components of i using a given detector is recorded at a given kV; the relative *Joshi-effect* is $\% \Delta i = \frac{\Delta i \times 100}{i_D}$. The ratios of different components of i in LT to i_{aerial} at the above mentioned kV are returned under (*a*) and (*b*) in Table I.

§ 3. During these observations the marked significance of the 'threshold potential' V_m[1,10] was noticed. V_m was found to be 4·3 kV irrespective of the nature of the detector[11] used and also of the current component measured. In agreement with previous results of Joshi,[12] it was in general found that $\% \Delta i$ was appreciably greater in i_{aerial} than in the rest of the

Fig 2. Joshi-effect in H.F., L.F. Regions of Discharge Current, Double Diode Detection

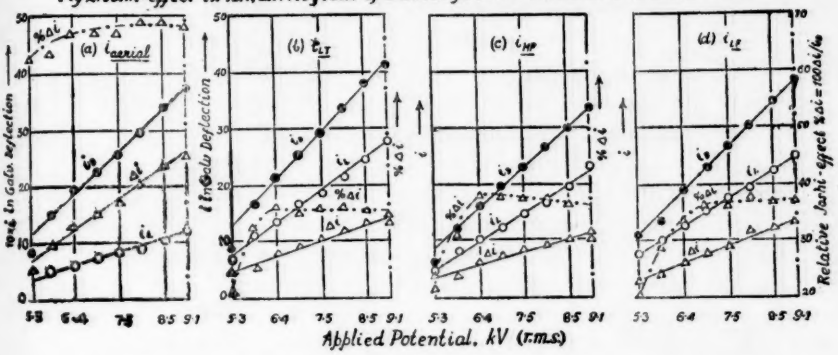


Fig 3. Joshi-effect in H.F., L.F. Regions of Discharge Current, Vacuo-Junction Detection

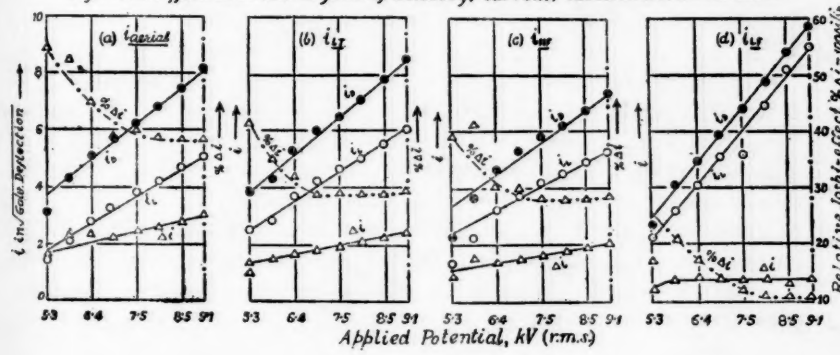


TABLE I

Potential Variation of i_{LT} *and its Components relative to* i_{aerial}

kV	(*a*) Detector–Double Diode 6H6						(*b*) Detector-Vacuo-Junction					
	Dark			Light			Dark			Light		
	$\frac{i_{LT}}{i_{aerial}}$	$\frac{i_{HF}}{i_{aerial}}$	$\frac{i_{LF}}{i_{aerial}}$	$\frac{i_{LT}}{i_{aerial}}$	$\frac{i_{HF}}{i_{aerial}}$	$\frac{i_{F}}{i_{aerial}}$	$\frac{i_{LT}}{i_{aerial}}$	$\frac{i_{HF}}{i_{aerial}}$	$\frac{i_{LF}}{i_{aerial}}$	$\frac{i_{LT}}{i_{aerial}}$	$\frac{i_{HF}}{i_{aerial}}$	$\frac{i_{LF}}{i_{aerial}}$
5·3	5·38	3·90	4·19	11·83	7·75	8·92	0·81	0·69	0·88	1·03	0·92	1·60
5·9	5·50	3·92	4·36	10·18	7·35	8·55	0·99	0·84	0·94	1·35	1·05	1·57
6·4	5·49	4·14	4·80	10·46	7·65	9·67	1·03	0·90	0·96	1·28	1·14	1·73
6·9	5·69	4·35	5·05	11·13	8·14	9·90	1·05	0·93	1·04	1·21	1·05	1·46
7·5	5·70	4·47	5·15	10·94	8·50	10·09	1·04	0·92	1·08	1·23	1·23	1·59
8·0	5·70	4·53	5·10	12·00	9·25	10·45	1·04	0·91	1·14	1·15	1·06	1·63
8·5	5·59	4·38	5·07	11·76	9·20	10·50	1·04	0·90	1·17	1·18	1·04	1·60
9·1	5·48	4·42	5·11	11·54	9·65	10·27	1·04	0·89	1·17	1·17	1·02	1·75

current, including even the HF component measured in the LT line with either of the above arrangements. Thus, for example, with the double diode, at 5·3 kV, $\%\Delta i$ was 62·5 and 24·2 in i_{aerial} and i_{HF} respectively. The decrease in $\%\Delta i$ at a given kV is in the order $i_{aerial} > i_{HF} > i_{LT} > i_{LF}$; this is also the order in respect of mean frequency. From Figs. 2 and 3, it is seen that an increase beyond V_m in the applied potential is found to increase i_D appreciably and also Δi; the corresponding $\%\Delta i$, however, decreases in the vacuo-junction detection,[13] but increases using the diode over only a limited range; at large kV, it is almost constant. It is interesting to observe that for the same difference in kV, percentage increase in i_D and Δi, and percentage variation in $\%\ \Delta i$ are larger near V_m than above it. Thus, *e.g.*, on changing from 5·3 to 6·4 kV, i_D and Δi increase from 2·1 to 4·6 and 0·8 to 1·4 respectively, while $\%\ \Delta i$ is reduced from 39 to 30, as compared with the variation from 8·0 to 9.1 kV; this latter increased i_D and Δi from 6·2 to 7·3 and 1·8 to 2·2 respectively; the corresponding $\%\ \Delta i$, however, remained practically, constant *viz.*, 28 [*cf.* Fig. 3 (*c*)]. Furthermore, the relative variation in $\%\ \Delta i$ is more pronounced in i_{LF} than that in i_{HF} for the same increase in kV; *e.g.*, with the vacuo-junction detection, for a change in kV from 5·9 to 9·1, the decrease in $\%\ \Delta i$ was 57% and 30% in i_{LF} and i_{HF} respectively. As suggested by Prof. Joshi, this is due to the comparative instability of the discharge[3, 19] near the threshold potential V_m; the corresponding large i and preponderance of the LF component of i at large kV (*vide infra*) are additional factors. The dependence, on the nature of the current detector employed, of the magnitude of Δi and $\%\ \Delta i$ in i_{LT} has been emphasised by Joshi.[9 13] This is illustrated by the results for i_{aerial}, i_{HF}, and i_{LF}; thus, *e.g.*, in i_{aerial}, at 9·1 kV, $\%\ \Delta i$ observed with the diode and the vacuo-junction was 68 and 37·3 respectively.

The results show that both i_D and Δi increases as kV increases over a certain range. It is to be anticipated therefore, that an increase in kV would decrease the ratio $\Delta i/i_D$ if relative increase in Δi is smaller than that in i_D; this has been actually observed. This would result if the increase in i_{LF} is larger than in the rest of the current components of the LT because it has been emphasised by Joshi that the chief seat of Δi lies in i_{HF}. It follows therefore, that the distribution of the various components, *viz.*, i_{aerial}, i_{HF}, i_{LF} and i_S, the last representing the supply component and its harmonics, depends upon the applied potential. This is further brought out by results in Table I (*a*) and (*b*) in which the ratios of various components of i_{LT} to i_{aerial} have been shown. It is significant that i_{LT}/i_{aerial}, i_{HF}/i_{aerial} and i_{LF}/i_{aerial} do not show any marked variations; i_{LF}/i_{aerial} is however, greater than i_{HF}/i_{aerial}, both in dark and light; furthermore, it

is much larger under irradiation. Since i_{aerial} is same, i_{LF}/i_{aerial} would be greater than i_{HF}/i_{aerial} at the same kV, if the relative proportion in the total i, of i_{LF} is greater than i_{HF}. It is suggested, therefore, that as kV increases i_{LF} preponderates. Furthermore, $i_L/(i_{aerial})_L$ is found to be greater than $i_D/(i_{aerial})_D$ irrespective of the current component measured in LT. This further supports Joshi's view that Δi originates chiefly in i_{HF}, since the low capacity aerial picks up the predominantly i_{HF} and that the current in LT consists mainly of i_{LF}.

In conclusion, we express our sincerest thanks to Professor S. S. Joshi D.Sc. (Lond.), F.A.Sc., for suggesting the problem and kind interest during the investigation.

Summary

The distribution of the total current i, as i_{aerial} which represents (owing to the low capacity of the aerial) the highest (mean) frequency; as i_{HF} and i_{LF}, the filtered high and low frequency parts of the tube current in the LT line has been studied in dark and in light at applied potentials varied in the range 5–9 kV, using a vacuo-junction and double diode as detectors. The relative *Joshi-effect* $\%\ \Delta i$, *i.e.*, the percentage photo-diminution of the current in dark in a given frequency region varies as $i_{aerial} > i_{HF} > i_{LT} > i_{LF}$, which is also the order in respect of their mean frequencies. The ' threshold potential ' V_m is found to be independent of the nature of both the detectors and also of the frequency regions; for each of these, $\%\ \Delta i$ is maximum near V_m. The decrease on increasing the applied potential, in $\%\ \Delta i$ is attributed to the corresponding preponderance of i_{LF} which is comparatively insensitive to the production of this phenomenon.

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THE STRUCTURE OF OZONE—AN INTERPRETATION OF ITS MAGNETIC SUSCEPTIBILITY

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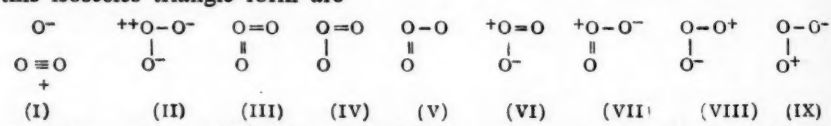
The structure of the ozone molecule has provided material for so many investigations that an addition to the literature may seem superfluous. The present communication is an attempt to correlate the various resonance structures with the observed magnetic susceptibility.

Using the method of electron diffraction, Shand and Spurr[7] obtained for the O–O bond distances and the O–O–O bond angle values consistent with the observations of Penney and Sutherland[5] that the molecule has a symmetrical angular form. The possible electronic structures consistent with this isosceles triangle form are



(I) (II) (III) (IV) (V) (VI) (VII) (VIII) (IX)

Of these structures I and II are unlikely as ozone does not show the characteristic properties of a highly polar substance. Penney and Sutherland consider that the O–O bonds have about 30% double-bond character with structures VI, VII, VIII and IX as the most important among the resonance structures.

It has been shown earlier[1] that in the case of carbon compounds, following the method of Gray,[2] bond depression values could be calculated for various bond types and an empirical curve correlating these bond depressions with bond orders could be obtained for C–C bonds. One may reasonably expect a similar relationship with other elements as well. A direct evaluation of bond depression values for O–O bonds is not feasible as the simplest molecule O_2 does not have a covalent double bond and the structure of hydrogen peroxide eliminates that compound as a standard for a single bond. Both values have consequently to be obtained by some form of extrapolation. This is possible if one were to assume that the paramagnetic contribution of a bond can be treated as a periodic property. The values for C–C bonds have been calculated (Anantakrishnan, *loc. cit.*) and by similar methods using hydrazo and azo benzene as standards, the bond depressions of the N–N bonds, single and double, can be obtained. As a first approximation, the difference between the carbon bonds and the nitrogen

bonds can be taken as the difference between the latter and the oxygen bonds. The values will then be as in Table I.

TABLE I

Nature of Bond	Bond depression value		
	Carbon-Carbon	Nitrogen-Nitrogen	Oxygen-Oxygen
Single bond ..	2·08	1·80	1·52
Double bond ..	7·68	5·0	2·3

Using these bond depression values and Slater's values for the atomic susceptibility of oxygen, the molar susceptibility of the different valence bond structures may be evaluated. The results are summarised in Table II.

TABLE II

All susceptibility values are in uuits of 10^{-6}

Structure	Susceptibility
IV and V ..	− 17·46
VI and VII ..	− 18·09
VIII and IX ..	− 18·89
III ..	− 16·66

All the possible valence structures thus appear to indicate that ozone should be diamagnetic. The careful work of Laine[3] makes out that the compound is a feebly paramagnetic substance with a susceptibility of $6.72 \pm 0.96 \times 10^{-6}$ (one experiment, however, appears to give a diamagnetic value). Wulf[9] and Vaidyanathan[8] working with ozonised oxygen make it out to be a diamagnetic compound. One obvious explanation for the discrepancy is the possible presence of molecular oxygen in the ozone studied. Also, it is necessary to consider possible deviations when considering measurements in liquids at the low temperatures used by Laine. In his experiments, Laine allows for the temperature dependent paramagnetism of oxygen and the key to the problem lies in a consideration of the high frequency paramagnetism of the two molecules, oxygen and ozone.

Van Vleck has shown that the molar susceptibility of oxygen can be calculated on the assumption that the multiplet structures are small compared to kT making the matrix elements of the spin essentially of the low frequency type. Rough calculation of $h^2/8\pi$L using existing spectroscopic data on ozone shows that this is much larger than T and the multiplet structure of ozone is also not of negligible width. Even with oxygen, where

these complications are relatively unimportant, the Leiden observations[6] have been shown by Van Vleck to require a consideration of high frequency elements. The position with ozone then becomes even more complex. A further difficulty in taking the observations in a liquid has also to be mentioned. Even with non-polar liquids, highly discrete spectra are rarely obtained and forbidden transitions often make their appearance, presumably involving a modification of the selection rules. Ellis and Kneser have found this to be the case with liquid oxygen. A small but definite dipole moment has been observed for the ozone molecule[4] and the polar nature of the liquid can be expected to modify to an even greater extent the spectroscopic behaviour. This will naturally be reflected in the matrix elements of the high frequency term. The possibility of differences between the liquid and gaseous states together with the difficulties involved in the accurate measurements can account for the range of values reported by different authors or even by the same worker.

The magnetic susceptibility value then does not enable any unequivocal decision about the contributing valence bond structures. At the same time, it is obvious that structures IV and V cannot be excluded, nor even structure III which gives the lowest diamagnetic susceptibility value. Lewis and Smyth[4] observe for ozone a dipole moment of $0{\cdot}49\times 10^{-18}$ e.s.u. and this is consistent with appreciable contributions by the three structures mentioned. Susceptibility values may then be considered to conform to what may be expected from other physical measurements.

Summary

Calculation of magnetic susceptibility for the different valence bond structures indicate that ozone should be diamagnetic, the susceptibility being about -18×10^{-6} while reported experimental values show that it is feebly paramagnetic in the liquid state, diamagnetic values being reported for the gaseous state. The possible causes of the discrepancy and a comparison with oxygen are discussed. The magnetic behaviour may be considered to conform to what may be expected from other physical properties of ozone.

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ZUR ABLEITUNG DES MAGNETISCHEN MOMENTS DES ELEKTRONS

By Von V. S. Vrkljan in Zagreb

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Bekanntlich gelang es vor atwa 18 Jahren dem britischen Forscher *P. A. M. Dirac*,[1] die fur die moderne Atomtheorie fundamentale Annahme des Elektronenspins auf relativitätstheoretischem Wege zu deduzieren. Zugleich wurde auf Grund dieser Theorie auch der Vert des magnetischen Moments des Elektrons richtig abgeleitet. Die dazu genügende Bedingung für die Lösung des Problems wurde von *Dirac* in der Einführung der vierreihigen quadratischen Matrizen α_β gefunden, welche die besondere Eigenschaft $[\alpha_\beta^2 = 1, \alpha_\beta \alpha_\gamma = -\alpha_\gamma \alpha_\beta (\beta, \gamma = 1, 2, 3, 4, \gamma \neq \beta)]$ erfüllen. Bei der Ableitung des magnetischen Momentes des Elektrons kann man indessen entweder (im Falle eines elektromagnetischen Feldes) ganz allgemein verfahren ohne weitere Spezialisierung der *Dirac*schen Matrizen[2] oder ohne Annahme der Anwesenheit des Magnetfeldes durch weitere Spezialisierung der Matrizen und mittels des Wellenpaketes von *C. G. Darwin*.[3] Bei dieser letzten Ableitung wurde—sofern mir bekanntist*—die Methode angewendet, dass man die Matrix vor dem Produkt $m_\circ c$ ($m_\circ$ ist die Ruhmasse des Elektrons, c die Lichtgeschwindigkeit im Vakuum) aus (reellen) Einheiten in der Hauptdiagonale Konstruiert. Auf diese Weise erhält man nämlich dieselbe Ψ-Funktion (Komponente des Spinors) bei $m_\circ c$ und in der Derivation $\frac{\partial \Psi}{\partial t}$, was bei den weiteren Berechnungen in der *Newton*schen Näherung zum Ausdruck $2m_\circ c$ führt, von welchen der Faktor 2 später zur Kürzung des Faktors 2 vor dem Ausdruck für den Konvektionsstrom und vor dem Ausdruck für den magnetischen Moment des Elektrons dient. Es könnte deshalb scheinen, als ob eine solche Konstruktion der Matrix für $m_\circ c$ notwendig wäre, um zu dem richtigen Werte des Konvektionsstromes und des magnetischen Momentes zu gelangen.

Der Zweck dieser Zeilen ist, zu zeigen, wie man mittels des Wellenpaketes von *C. G. Darwin* auch die Werte des Konvektionsstromes und des magnetischen Momentes erhalten kann, wenn die Konstruktion der Matrix

* Die ganze britische und amerikanische wissenschaftliche Literatur während des Krieges und teilweise auch vor dem Kriege ist mir unzugänglich.

α_4 vor $m_\circ c$ eine solche wird, dass neben $m_0 c$ und in $\frac{\partial \Psi}{\partial t}$ verschiedene Ψ-Funktionen auftreten. Zum Schluss wird dann explizite die Konstruktion einer unendlichen Anzahl von Matrizen α_4 gezeigt, die alle zu dem richtigen Wert des Konvektionsstromes und des magnetischen Momentes führen.

Wir setzen also als *Dirac*sche Matrizen zuerst

$$\alpha_1=\begin{vmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{vmatrix} \quad \alpha_2=\begin{vmatrix} 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{vmatrix} \quad \alpha_4=\begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix} \quad \alpha_4=\begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix} \tag{1}$$

unter welchen drei (α_1, α_2 und α_4), wie man sieht, gleichzeitig aus reellen sowie imaginären Einheiten konütruiert sind. Schreiben wir jetzt, wie üblich, die "linearisierte" Hamilton-Jacobische Differentialgleichung der Relativitätstheorie für eine Partikel im feldlosen Falle

$$\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z + \alpha_4 m_\circ c - \mathbf{1}\frac{U}{c} = 0 \tag{2}$$

wo p_x, p_y und p_z die Impulskomponenten und U die Energie der Partikel bedeutet (h ist die Plancksche Wirkungskonstante) und führen wir die bekannte Substitution $p_x \rightarrow \frac{h}{2\pi i}\frac{\partial}{\partial x}$, $p_y \rightarrow \frac{h}{2\pi i}\frac{\partial}{\partial y}$, $p_z \rightarrow \frac{h}{2\pi i}\frac{\partial}{\partial z}$, $U \rightarrow -\frac{h}{2\pi i}\frac{\partial}{\partial t}$ ein und lassen wir diese Operatoren auf eine Funktion Ψ wirken, so erhalten wir die vier Gleichungen

$$\left.\begin{aligned}
&\frac{h}{2\pi i}\left\{-\frac{\partial \Psi_2}{\partial x}+i\frac{\partial \Psi_2}{\partial y}+\frac{\partial \Psi_1}{\partial z}\right\}+m_0 c\,\Psi_4+\frac{h}{2\pi i c}\cdot\frac{\partial \Psi_1}{\partial t}=0\\
&\frac{h}{2\pi i}\left\{-\frac{\partial \Psi_1}{\partial x}-i\frac{\partial \Psi_1}{\partial y}-\frac{\partial \Psi_2}{\partial z}\right\}+im_0 c\,\Psi_3+\frac{h}{2\pi i c}\cdot\frac{\partial \Psi_2}{\partial t}=0\\
&\frac{h}{2\pi i}\left\{-i\frac{\partial \Psi_4}{\partial x}+\frac{\partial \Psi_4}{\partial y}+\frac{\partial \Psi_3}{\partial z}\right\}-im_0 c\,\Psi_2+\frac{h}{2\pi i c}\cdot\frac{\partial \Psi_3}{\partial t}=0\\
&\frac{h}{2\pi i}\left\{i\frac{\partial \Psi_3}{\partial x}+\frac{\partial \Psi_3}{\partial y}-\frac{\partial \Psi_4}{\partial z}\right\}+m_3 c\,\Psi_1+\frac{h}{2\pi i c}\cdot\frac{\partial \Psi_4}{\partial t}=0
\end{aligned}\right\} \tag{3}$$

Multipliziert man diese Gleichungen mit $\frac{2\pi i}{h}$ und dann der Reihe nach mit den konjugiert-komplexen Spinoren $\dot{\Psi}_1$ $\dot{\Psi}_2$, $\dot{\Psi}_3$ und $\dot{\Psi}_4$, und umgekehrt, multipliziert man die zu den Gelichungen (3) konjugiert-komplex aufgeschriebene Gleichungen mit Ψ_1, Ψ_2, Ψ_3 und Ψ_4 und addiert alle diese Gleichungen,

so erhält man bekanntlicherweise [zudem nach Multiplikation der Summe mit ϵc, wo ϵ im allgemeinen (also ohne Rücksicht auf das Vorzeichen) die elektrische Ladung der Partikel bedeutet] eine der Kontinuitätsformel entsprechende Gleichung, aus der man sofort die Ausdrücke

$$\begin{aligned} j_x &= \epsilon c \left(-\dot{\Psi}_1\Psi_2 - \dot{\Psi}_2\Psi_1 - i\,\dot{\Psi}_3\Psi_4 + i\,\dot{\Psi}_4\Psi_3\right) \\ j_y &= \epsilon c \left(i\,\dot{\Psi}_1\Psi_2 - i\,\dot{\Psi}_2\Psi_1 + \dot{\Psi}_3\Psi_4 + \dot{\Psi}_4\Psi_3\right) \\ j_z &= \epsilon c \left(\dot{\Psi}_1\Psi_1 - \dot{\Psi}_2\Psi_2 + \dot{\Psi}_3\Psi_3 - \dot{\Psi}_4\Psi_4\right) \end{aligned} \tag{4}$$

als Komponenten der Stromdichte des Wahrscheinlichkeitsstromes erhält.

Um das magnetische Moment des Elektrons zu berechnen, müssen wir die Ausdrücke der Komponenten Ψ_1, Ψ_2, Ψ_3, Ψ_4 und $\dot{\Psi}_1$, $\dot{\Psi}_2$, $\dot{\Psi}_3$ $\dot{\Psi}_4$ des Spinors kennen und dieselben in das Gleichungssystem (4) einsetzen. Zu diesem Zweck müssen wir bekanntlicherweise zwei von den Komponenten des Spinors durch zwei andere ausdrücken; aus den Gleichungssystem (3) erkennen wir, dass dies möglich ist: d. h., wir können die Komponenten Ψ_1 und Ψ_2 des Spinors durch die Komponenten Ψ_3 und Ψ_4 ausdrucken ; oder umgekehrt, man kann auch die Komponenten Ψ_3 und Ψ_4 des Spinors durch Ψ_1 und Ψ_2 ausdrucken. Entschliessen wir uns für die erste Möglichkeit und beachten wir den bekannten *Darwin*schen Ausdruck[4] für $\Psi_{3,4}$, den wir für Zei $t = 0$ aufschreiben

$$\Psi_{3,4} = A_{3,4}\, e^{-\frac{x^2+y^2+z^2}{2R^2}} \cdot e^{\frac{2\pi i}{h}(p_x x + p_y y + p_z z)} = A_{3,4} \cdot P \tag{5}$$

wo R die " praktische " Ausdehnung des Wellenpaketes bedeutet, so erhalten wir aus den ersten zwei Gleichungen (3) in Newtonscher Näherung $\left(\frac{U}{c} \doteq m_0 c\right)$ folgende Formeln für Ψ_1 und Ψ_2

$$\begin{aligned} \Psi_1 &= \left\{\frac{1}{m_0 c}\left[A_3(-ip_x - p_y) + A_4 p_z + \frac{h}{2\pi}\cdot\frac{A_3(x-iy) + A_4 iz}{R^2}\right] + A_4\right\} P \\ \Psi_2 &= \left\{\frac{1}{m_0 c}\left[A_4(-p_x - ip_y) - A_3 \cdot ip_z + \frac{h}{2\pi}\cdot\frac{A_4(-ix+y) + A_3 z}{R^2}\right] + iA_3\right\} P \end{aligned} \tag{6}$$

Wie wir sofort ersehen, unterscheiden sich diese Ausdrücke für Ψ_1 und Ψ_2 von den bis jetzt verwendeten[5] durch die Zusatzglieder A_4 bzw. iA_3, welche jetzt bewirken, dass die Funktionen Ψ_1, Ψ_2, Ψ_3 und Ψ_4 jetzt nicht, wie bei früheren Berechnungen, in " kleine " und " grosse " geteilt werden können, sondern alle von derselben Grössenordnung sind, falls solche Ψ_3 und Ψ_4 sind. Führt man die Ausdrücke für Ψ_1, Ψ_2, Ψ_3 und Ψ_4 aus (5) und

(6) in (4) ein, so erhält man unter Vernachlässigung der Ausdrücke mit $m_0^2c^2$ im Nenner

$$\begin{aligned}
j_x &= \frac{2\epsilon}{m_\circ}\left\{(\dot{A}_3A_3+\dot{A}_4A_4)\,m_\circ v_x+\frac{h}{4\pi}\Big[(\dot{A}_4A_4-\dot{A}_3A_3)\,\frac{\partial}{\partial y}\right.\\
&\qquad\left.-(-\dot{A}_4A_3-\dot{A}_3A_4)\,\frac{\partial}{\partial z}\Big]\right\}e^{-\frac{x^2+y^2+z^2}{R^2}}\\
j_y &= \frac{2\epsilon}{m_\circ}\left\{(\dot{A}_3A_3+\dot{A}_4A_4)m_\circ v_y+\frac{h}{4\pi}\Big[i\,(A_3\dot{A}_4-\dot{A}_4A_3)\,\frac{\partial}{\partial z}\right.\\
&\qquad\left.-i\,(\dot{A}_4A_4-\dot{A}_3A_3)\,\frac{\partial}{\partial x}\Big]\right\}e^{-\frac{x^2+y^2+z^2}{R^2}} \qquad (7)\\
j_z &= \frac{2\epsilon}{m_\circ}\left\{(\dot{A}_3A_3+\dot{A}_4A_4)\,m_0v_z+\frac{h}{4\pi}\Big[-\dot{A}_3A_4-\dot{A}_4A_3)\,\frac{\partial}{\partial x}\right.\\
&\qquad\left.-i\,(\dot{A}_3A_4-\dot{A}_4A_3)\,\frac{\partial}{\partial y}\Big]\right\}e^{-\frac{x^2+y^2+z^2}{R^2}}
\end{aligned}$$

Definieren wir jetzt mittels der Gleichungen

$$\left.\begin{aligned}
\frac{1}{4\pi}\,T_x &= 2\,\frac{\epsilon h}{4\pi m_0c}\,i(\dot{A}_3A_4-\dot{A}_4A_3)\\
\frac{1}{4\pi}\,T_y &= 2\,\frac{\epsilon h}{4\pi m_0c}\,(-\dot{A}_3A_4-\dot{A}_4A_3)\\
\frac{1}{4\pi}\,T_z &= 2\,\frac{\epsilon h}{4\pi m_0c}\,(\dot{A}_4A_4-\dot{A}_3A_3)
\end{aligned}\right\}e^{-\frac{x^2+y^2+z^2}{R^2}} \qquad (8)$$

einen Vektor $\vec{T}$, so erhalten wir leicht mittels der Formel aus Elektromagnetismus

$$\vec{M}=\frac{1}{4\pi}\int\vec{T}\,d\tau$$

folgende Gleichungen

$$\begin{aligned}
M_x &= 2\,\frac{\epsilon h}{4\pi m_0c}\,i\,(\dot{A}_3A_4-\dot{A}_4A_3)\int e^{-\frac{x^2+y^2+z^2}{R^2}}\,d\tau\\
M_y &= 2\,\frac{\epsilon h}{4\pi m_0c}\,(-\dot{A}_3A_4-\dot{A}_4A_3)\int e^{-\frac{x^2+y^2+z^2}{R^2}}\,d\tau \qquad (10)\\
M_z &= 2\,\frac{\epsilon h}{4\pi m_0c}\,(\dot{A}_4A_4-\dot{A}_3A_3)\int e^{-\frac{x^2+y^2+z^2}{R^2}}\,d\tau
\end{aligned}$$

wo die Integrale über den ganzen Raum zu erstrecken sind. Hier haben wir nur noch die Normierung auszuführen und dies ergibt

$$\int(\dot{\Psi}_1\Psi_1+\dot{\Psi}_2\Psi_2+\dot{\Psi}_3\Psi_3+\dot{\Psi}_4\Psi_4)\,d\tau=1 \qquad (11)$$

oder nach Berüchksichtigung der Formeln (5) und (6) und Hinstreichen der Ausdrucke wo $m_0 c$ oder $m_0{}^2c^2$ im Nenner vorkommt,

$$2\,(\dot{A}_3 A_3 + \dot{A}_4 A_4) \int e^{-\frac{x^2+y^2+z^2}{R^2}}\, d\tau = 1 \tag{12}$$

Mit Rucksicht auf die Normierungsgleichung (12) erhalten wir endlich aus (10) fur den Absolutwert des magnetischen Momentes des Elektrons (und auch des Positrons).

$$|\,M\,| = \frac{\epsilon h}{4\pi m_0 c}. \tag{13}$$

Es ist noch zu bemerken, dass durch Normierungsgleichung (12) zugleich die Normiwerung des Ausdruckes für den Konvektionsstrom in den Gleichungen (7) durchgeführt ist.

Jetzt wenden wir uns zu der zweiten Aufgabe dieser Abhandlung, nämlich zur Konstruktion einer unendlichen Anzahl von Matrizen a_4, welche alle mittels des Wellenpaketes von *C. G. Darwin* zu dem magnetischen Moment des Elektrons führen. Es sind dies die Matrizen

$$a_1 = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix} \quad a_2 = \begin{vmatrix} 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{vmatrix} \quad a_3 = \begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix} \quad a_4 = \begin{vmatrix} 0 & 0 & \frac{\sqrt{n}+i}{\sqrt{(n+1)}} & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{n}-i}{\sqrt{(n+1)}} \\ \frac{\sqrt{n}-i}{\sqrt{(n+1)}} & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{n}+i}{\sqrt{(n+1)}} & 0 & 0 \end{vmatrix} \tag{14}$$

wo n eine beliebige natürliche Zahl bedeutet. Für $n = 0$ würde die Matrix a_4 in die bis jetzt (d. h. vor dieser Abhandlung) verwandete Form übergehen. Auf Grund dieser Matrizen erhält man 4 Gleichungen, die durch analoges Verfahren wie früher zu den Formeln

$$j_x = \epsilon c\,(\dot{\Psi}_1\Psi_1 + \dot{\Psi}_2\Psi_2 - \dot{\Psi}_3\Psi_3 - \dot{\Psi}_4\Psi_4)$$

$$j_y = \epsilon c i\,(\dot{\Psi}_1\Psi_4 + \dot{\Psi}_2\Psi_3 + \dot{\Psi}_3\Psi_2 - \dot{\Psi}_4\Psi_1)$$

$$j_z = \epsilon c\,(\dot{\Psi}_1\Psi_4 + \dot{\Psi}_1\Psi_3 + \dot{\Psi}_3\Psi_2 + \dot{\Psi}_4\Psi_1)$$

für die Stromdichte des Wahrscheinlichkeitsstromes führen. Von den erwähnten 4 Gleichungen sind es die erste und die vierte, aus denen man die wellenmechanischen Funktionen Ψ_2 und Ψ_3 durch Ψ_1 und Ψ_4 ausdrücken kann und umgekehrt, aus der zweiten und dritten die Funktionen Ψ_1 und Ψ_4 durch Ψ_2 und Ψ_3. Entschliessen wir uns für die zweite Möglichkeit,

so erhalten wir

$$\Psi_1=\frac{\sqrt{n}+i}{\sqrt{n+1}}\left\{\frac{1}{m_0c}\left[A_3\,p_x+A_2(-ip_y+p_z)+\frac{h}{2\pi}\cdot\frac{A_3ix+A_2(y-iz)}{R^2}\right]+A_3\right\}P \tag{16}$$

$$\Psi_2=\frac{\sqrt{n}+i}{\sqrt{n+1}}\left\{\frac{1}{m_0c}\left[A_2\,p_x+A_3(-ip_y+p_z)+\frac{h}{2\pi}\cdot\frac{A_2ix+A_3(y+iz)}{R^2}\right]-A_2\right\}P$$

Durch Einführung dieser Ausdrücke in (15) erhält man

$$j_x=2\Big\{(\dot{A}_2A_2+\dot{A}_3A_3)\,\epsilon v_x+\frac{\epsilon h}{4\pi m_0}\Big[(-\dot{A}_2A_3-\dot{A}_3A_2)\,\frac{\partial}{\partial y}$$
$$-i\,(\dot{A}_2A_3-\dot{A}_3A_2)\,\frac{\partial}{\partial z}\Big]\Big\}\,e^{-\frac{x^2+y^2+z^2}{R^2}}$$

$$j_y=2\Big\{(\dot{A}_2A_2+\dot{A}_3A_3)\,\epsilon v_x+\frac{\epsilon h}{4\pi m_0}\Big[(\dot{A}_3A_3-\dot{A}_2A_2)\,\frac{\partial}{\partial z}$$
$$-(-\dot{A}_2A_3-\dot{A}_3A_2)\,\frac{\partial}{\partial x}\Big]\Big\}\,e^{-\frac{x^2+y^2+z^2}{R^2}} \tag{17}$$

$$j_z=2\Big\{(\dot{A}_2A_2+\dot{A}_3A_3)\,\epsilon v_z+\frac{\epsilon h}{4\pi m_0}\Big[i\,(\dot{A}_2A_3-\dot{A}_3A_2)\,\frac{\partial}{\partial x}$$
$$-(\dot{A}_3A_3-\dot{A}_2A_2)\,\frac{\partial}{\partial y}\Big]\Big\}\,e^{-\frac{x^2+y^2+z^2}{R^2}}$$

welche Gleichungen, wie man ersieht, vollkommen analoge Form wie die Formeln (7) haben und deswegen zu den gleichen Resultaten führen.

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THE STRONGEST TOPOLOGY ON A LINEAR SPACE SUBJECT TO GIVEN CONDITION*

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Introduction

Anticipating the definitions and explanations given below, and denoting by $T_0(E; F)$ the strongest topology on a linear space E subject to the condition that a given total family of linear functionals defined on E should be continuous, the following are the main results of this paper:—

(1) $T_0(E; F)$ is a convex topological linear space which cannot be normed except when the space E is finite dimensional.

(2) If the family F is enumerably infinite, then $T_0(E; F)$ is metrisable with an F-metric.

(3) If in addition there exists at least one norm on E such that the functionals of F are continuous in the corresponding normed topology, then $T_0(E; F)$ is the lattice-product of a specified class of normed topologies satisfying the same condition. The cardinal number of the set of such normed topologies required to get the lattice-product is more than enumerable but does not exceed the cardinal number of the continuum.

1.1. *Norms on a Linear Space.*—Let E be a linear space.[1] A non-negative quantity $|\alpha|$ associated with each element $\alpha \in E$ is called a norm on E if the following conditions are satisfied (B, p. 53):—

(i) $|\Theta| = 0$ where Θ is the zero element of E and $|\alpha| > 0$ if $\alpha \neq \Theta$.

(ii) $|\alpha + \beta| \leqslant |\alpha| + |\beta|$

(iii) $|a\alpha| = |a|\,|\alpha|$ where a is any real number.

The topology induced on E by the metric $\rho(\alpha, \beta) = |\alpha - \beta|$ will be called a normed topology and will be denoted by $N(E; |\alpha|)$.

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* The subject-matter of this paper is based on the problem [see the example (1) in § 4] for the Narasinga Rao Gold Medal proposed by the Indian Mathematical Society in 1945.

[1] For the definition of a linear space, see Banach, "Operations Lineaires" (*Monografje Math.*, Tom. 1, Warsaw, 1932). This will be referred to as "B" in the sequel.

1.2. *Linear Functionals on E.*—A real-valued function $f(\alpha)$ defined on E is said to be additive on E if $f(\alpha+\beta)=f(\alpha)+f(\beta)$. It is said the homogeneous if $f(a\alpha)=af(\alpha)$. If $f(\alpha)$ is additive and homogeneous it will be called linear. It is known (*B*, pp. 54–55) that if an additive functional $f(\alpha)$ is continuous with respect to a normed topology $N(E;|\alpha|)$ then it is homogeneous and that there exists a finite positive number M such that $|f(\alpha)| \leqslant M|\alpha|$. The least value of M for which this is true, is easily seen to be $\max_{|\alpha|\leqslant 1} \frac{|f(\alpha)|}{|\alpha|}$ and is called the norm of the functional.

1.3. *The Lattice of all Topologies.*—Let E be a linear space and F a family of linear functionals on E. We shall denote by $\Gamma(E;F)$ the set of all T_1-topologies[2] on E such that each functional of F is continuous in these topologies. If we define $T_1 \leqslant T_2$ to mean that the topology T_1 is stronger[3] than T_2, then it is known that $\Gamma(E;F)$, thus partially ordered, is a complete lattice.[4] Hence the smallest element $T_0(E;F)$ of $\Gamma(E;F)$ exists and is the strongest topology on E subject to the condition that each functional of the family F is continuous in the topology. The object of this paper is to discuss some properties of $T_0(E;F)$. We shall use the symbol $T_1 < T_2$ to denote that T_1 is actually stronger than T_2, *i.e.*, $T_1 \leqslant T_2$ but T_1 is not equivalent to T_2.

1.4. We shall conclude the introduction by proving the following two lemmas on the comparison of normed topologies.[5]

LEMMA 1.—*Let E be a linear space. Let* $N(E;|\alpha|_1)$ *and* $N(E;|\alpha|_2)$ *be two normed topologies on E corresponding to the norms* $|\alpha|_1$ *and* $|\alpha|_2$. *A necessary and sufficient condition that* $N(E;|\alpha|_1) \leqslant N(E;|\alpha|_2)$ *is that there exists a finite positive number M such that* $|\alpha|_1 \leqslant M|\alpha|_2$ *for all* $\alpha \in R$.

Proof.—Since both $N(E;|\alpha|_1)$ and $N(E;|\alpha|_2)$ are linear metric spaces, $N(E;|\alpha|_1) \leqslant N(E;|\alpha|_2)$ if and only if $|\alpha_n|_2 \to 0$ as $n \to \infty$ for a sequence (α_n) of elements of E, implies that $|\alpha_n|_1 \to 0$ as $n \to \infty$. Hence it is obvious that the condition is sufficient. To prove that it is necessary, suppose that $|\alpha|_1/|\alpha|_2$ is unbounded as α varies over E. Then we can find a sequence (α_n) such that $|\alpha_n|_1/|\alpha_n|_2 \to \infty$ as $n \to \infty$ By multiplying

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[2] See, Alexandroff and Hopf, *Topologie*, p. 59.

[3] In the sense Alexandroff and Hopf, *l.c.*, p. 62.

[4] For the definition of a complete lattice, see G. Birkhoff, *Lattice Theory* (Amer. Math. Sos. Coll. Publications, vol. 25), p. 17; also, *Fundamenta Mathematica*, 26, 156–166.

[5] A referee points out that the results of the two lemmas and some other results of this paper are known. But I am unable to give definite references.

the numerator and denominator of $|\alpha_n|_1/|\alpha_n|_2$ by suitable constants [which does not alter the value of the ratio, by property (iii) of the norm, § 1.1] we can suppose that $|\alpha_n|_1 = 1$ for all n. But then $|\alpha_n|_1/|\alpha_n|_2 \to \infty$ implies that $|\alpha_n|_2 \to 0$ as $n \to \infty$ while $|\alpha_n|_1 (= 1$ for all $n)$ does not tend to zero. So N (E; $|\alpha|_1$) is not stronger than N (E; $|\alpha|_2$). This proves the lemma.

1.5. LEMMA 2.—*Let* $N(E; |\alpha|_1)$ *and* $N(E; |\alpha|_2)$ *be two normed topologies on E. A necessary and sufficient condition that these two should be equivalent is that there exist positive numbers m and M such that* $m|\alpha|_2 \leqslant |\alpha|_1 \leqslant M|\alpha|_2$ *for all* $\alpha \epsilon E$. *The relation* $N(E; |\alpha|_1) < N(E; |\alpha|_2)$ *is true if and only if* $|\alpha|_1 \leqslant M|\alpha|_2$ *while* $\min_{\alpha \epsilon E} |\alpha|_1/|\alpha|_2 = 0$.

These are immediate consequences of lemma 1.

Remark.—The result due[6] to Fichtenholz, that two normed topologies on E are equivalent if and only if any linear functional continuous in one topology is also continuous in the other, is an immediate consequence of the first part of lemma 2 and the property of such a functional mentioned in §1.2.

2. In what follows we shall suppose that the family F of linear functionals are linearly independent, since if any finite number of functionals be continuous in a topology on E, then any linear combination of these is also continuous.

THEOREM 1.—*Let E be any linear space and F a total family of linear functionals on E. Let* $(f_1, f_2, \ldots f_p)$ *be any finite set of functionals of F and let* $U(f_1, f_2, \ldots f_p; \delta)$ *denote that set of all elements* α *of E satisfying the relation.*

$$|f_n(\alpha)| < \delta, \quad n = 1, 2, \ldots p \tag{1}$$

where $\delta > 0$. *Let* $\Sigma(\Theta)$ *denote the set of all such* U^s *obtained for all finite selection of functionals of F and for all* $\delta > 0$. *These are assigned as the neighbourhoods of* Θ *and the neighbourhoods of any element* α *of E are obtained by translation of* $\Sigma(\Theta)$. *This system of neighbourhoods of the elements of E determines a topology* $T_0(E; F)$ *which is the strongest topology on E subject to the condition that each functional of F is continuous in the topology.* $T_0(E; F)$ *is a convex topological linear space.*[7]

[6] Fichtenholz, *Rec. Math* (*Mat. Sbornik*), N. S. 4 (1938), pp. 192–213. This reference is not available to the author.

[7] J. v. Neumann, "On Complete Topological Linear Spaces, *Trans. Amer. Math. Soc.*, 37, 1–20.

Proof.—It is easily verified that the system $\Sigma(\Theta)$ of neighbourhoods of Θ satisfy the postulates given by J. v. Neumann[8] for a convex topological linear space. It is also obvious that each functional of F is continuous in $T_0(E; F)$. Hence it remains only to show that if T is any topology on E such that the functionals of F are continuous, then $T_0(E; F) \leqslant T$. To prove this, let $U(f_1, \ldots . f_p; \delta)$ be a neighbourhood of $T_0(E; F)$. By hypothesis, there exists neighbourhoods $U_n(\alpha)$, $n = 1, 2, \ldots . p$, of α in T such that

$$| f_n(\beta - \alpha) | < \delta \text{ if } \beta \epsilon U_n(\alpha) \tag{2}$$

If $U(\alpha) = \prod_1^p U_n(\alpha)$, it follows from (2) that $U(\alpha) \subset U(f_1, f_2, \ldots . f_p; \delta) + \alpha$. So the theorem is proved.

2.1. THEOREM 2.—*The topology $T_0(E; F)$ of theorem* 1 *is not normable except when E is finite dimensional.*

The proof of this theorem requires the following known result[9] which we state in the form of a lemma.

2.2. LEMMA 3.—*A linear space E possesses a finite total set of functionals if and only if E is finite dimensional.*

2.3. *Proof of theorem* 2.—Suppose that E is not finite dimensional. Let $(f_1, f_2, \ldots . f_p)$ be any finite collection of functionals of F. Let $(\alpha_1, \alpha_2, \ldots . \alpha_n)$, $n > p$, be n linearly independent elements of E. Then, since $n > p$, we can find numbers $(x_1, x_2, \ldots . x_n)$ not all zero such that

$$x_1 f_i(\alpha_1) + x_2 f_i(\alpha_2) + \ldots . + x_n f_i(\alpha_n) = 0$$

for $i = 1, 2, \ldots . p$. If $\beta = x_1 \alpha_1 + x_2 \alpha_2 + \ldots . + x_n \alpha_n$ then $\beta \neq \Theta$ while

$$f_i(\beta) = 0, \; i = 1, 2, \ldots . p. \tag{3}$$

Now suppose that $T_0(E; F)$ is normable and that $| \alpha |$ is the norm. Then given ϵ we can find $\delta > 0$ and $(f_1, f_2, \ldots . f_p)$ of F such that

$$| \alpha | < \epsilon \text{ if } \alpha \epsilon U(f_1, f_2 \ldots . f_p; \delta) \tag{4}$$

Let $\beta \neq \Theta$ be an element satisfying (3) so that β as well as $a\beta$, a any real number, belongs to $U(f_1, f_2 \ldots . f_p; \delta)$. Hence $| a\beta | < \epsilon$ for any a. Letting $a \to \infty$ we see that $| \beta | = 0$ contrary to hypothesis. So if E is not finite dimensional, it is not normable.

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[8] J. v. Neumann, *l.c.*, p. 4.

[9] J. V. Wehansan, *Duke Math. Jour.*, 4, 167.

If E is finite dimensional, then the family F contains a finite total set $(f_1, f_2, \ldots . f_p)$ of functionals, by lemma 3. By rejecting some if necessary we can suppose these functionals to be linearly independent. It is now easy to verify that $|\alpha| = \max_{1 \leqslant n \leqslant p} |f_n(\alpha)|$ is a norm on E giving a topology, equivalent to $T_0(E; F)$ and that every other linear functional continuous in $T_0(E; F)$ is a linear combination of $(f_1, f_2, \ldots . f_p)$. This completes the proof.

3. In general $T_0(E; F)$ is not metrisable [see §4, (2)]. But if the family F is enumerably infinite, $T_0(E; F)$ is metrisable with a metric having the property (*B*, p. 35) $\rho(\alpha, \beta) = \rho(\alpha - \beta, \Theta)$, as is shown by the following theorem the proof of which is on the same lines as that of the result that the direct product topology of the st. line an enumerable number of times is metrisable.

THEOREM 3.—*If the total family F of linear functionals on E is enumerable and consists of the functionals* $(f_1, f_2, \ldots .)$ *then* $T_0(E; F)$ *is metrisable, the metric* $\rho(\alpha, \beta)$ *being given by*

$$\rho(\alpha, \beta) = \sum_{n=1}^{\infty} \frac{1}{2^n} \frac{|f_n(\alpha - \beta)|}{1 + |f_n(\alpha - \beta)|}.$$

Remark.—Theorem 4 remains true even if F is not enumerable but is equivalent to an enumerable family F_1 in the sense that the topologies $T_0(E; F)$ and $T_0(E; F_1)$ are equivalent.

4. We now proceed to the two main results of this paper. Let F be an enumerable family of linear functionals on E and let there exist at least[10] one normed topology $N(E; |\alpha|)$ on E in which the functionals $(f_1, f_2 \ldots .)$ of F are continuous. Then by §1.2 there exists a sequence of positive numbers $(k_1, k_2, \ldots .)$ such that

$$|f_n(\alpha)| \leqslant |k_n| \alpha |, \alpha \epsilon E. \tag{5}$$

If we put $g_n(\alpha) = f_n(\alpha)/k_n$, then it is obvious that that the families $(f_1, f_2, \ldots .)$ and $(g_1, g_2, \ldots .)$ are equivalent. If now, $(p_1, p_2, \ldots .)$ be a sequence of increasing positive numbers, it is easily seen that

[10] This is not a superfluous hypothesis. For instance, let s be the space of all real number sequences $\alpha = (a_1, a_2, \ldots .)$ and $f_n(\alpha) = a_n$, $n = 1, 2, \ldots .$ If there exists a norm $|\alpha|$ for which $(f_1, f_2, \ldots .)$ are continuous, then there exists numbers $(k_1, k_2, \ldots .)$ independent of α such that $\left(\frac{a_1}{k_1}, \frac{a_2}{k_2}, \ldots .\right)$ is a bounded sequence for all α. But this is not true if $\alpha = (k_1, 2k_2, 3k_3, \ldots .)$. Hence there exists no norm on s for which the total family $(f_1, f_2, \ldots .)$ is continuous.

$\max_{1 \leqslant n < \infty} \frac{|g_n(a)|}{p_n}$ is a norm on E such that the functionals of F are continuous. We shall denote this topology by N (E; p_n). If ($p_1, p_2, \ldots$) be a sequence of increasing positive integers, the corresponding topology will be called regular and will be denoted by RN (E; p_n). The set of all such normed topologies will be denoted by N (E; F) and that of regular normed topologies by RN (E; F). Both these are subsets of Γ (E; F). We shall now prove that T_0 (E; F) cannot be the lattice-product of any enumerable collection of normed topologies of N (E; F) but is the lattice product of all the topologies of RN (E; F) whose cardinal number does not exceed that of the continuum (see theorems 4 and 5).

3.2. THEOREM 4. *Let F be a total enumerable family of linear functionals on E an infinite dimensional linear space. Then T_0 (E; F) cannot be the lattice-product of any enumerable set of normed topologies of N (E; F).*

Proof.—If N (E; F) is empty the result is trivial. So we may suppose that there exists at least one topology in N (E; F). In view of theorems 1 and 2, it is enough to prove the following lemma to complete the proof of theorem 5.

LEMMA 4.—*Given any enumerable collection of topologies of N (E; F) there exists a topology of N (E; F) stronger than each member of this collection.*

Proof.—Firstly, we note that given any normed topology N (E; $|\alpha|$) of N (E; F), we can find a topology of RN (E; F) stronger than N (E; $|\alpha|$) To see this, let ($g_1, g_2, \ldots$) be the functionals equivalent to F as in §3.1. Since these are continuous in N (E; $|\alpha|$) we can find a sequence ($k_1, k_2, \ldots$) of positive numbers such that $|g_n(a)| \leqslant k_n |\alpha|$, $n = 1, 2, \ldots$. If we choose sequence of increasing positive integers ($p_1, p_2, \ldots$) such that $k_n = o(p_n)$, then, by lemma 1, the regular normed topology N (E; p_n) is stronger than the given one. So in proving the lemma we can suppose that each topology of the enumerable collection is regular. Let ($N_1, N_2, \ldots$) be these topologies and let ($p_{i1}, p_{i2}, \ldots$) be the sequence of positive integers, associated with N_i, $i = 1, 2, \ldots$. By a well-known theorem on orders of infinity, we can find a sequence ($p_1, p_2, \ldots$) of increasing positive integers such that $p_{in}/p_n \to 0$ as $n \to \infty$ for each $i = 1, 2, \ldots$. By lemma 1, the topology RN (E; p_n) is stronger than any member of the given collection.

3.3. THEOREM 5. *Let E be a linear space of infinite dimensions. Let $F = (f_1, f_2, \ldots)$ be a total enumerable family of linear functionals on E. Then*

the topology $T_0(E; F)$ is the lattice-product of all the topologies of $RN(E; F)$. Moreover, if $A \subset E$, then

$$(\bar{A})_{T_0} = \sum_{N \in RN(E; F)} (\bar{A})_N,$$

where $(\bar{A})_T$ is the closure of A in the topology T.

Proof.—By theorem 1, any topology in RN (E; F) is weaker than $T_0(E; F)$. Hence if T is the lattice-product of the topologies of RN (E; F) and A any subset of E, we get

$$(\bar{A})_{T_0} \supset (\bar{A})_T \supset \sum_{N \in RN(E; F)} (\bar{A})_N \tag{6}$$

by the definition of lattice-product and that of weaker and stronger topologies. Hence to prove the theorem it is enough to show that if $a \in (\bar{A})_{T_0}$ then there exists $N \in RN(E; F)$ such that $a \in (\bar{A})_N$. Since $T_0(E; F)$ is metrisable by theorem 4, $a \in (\bar{A})_{T_0}$ if and only if there exists a sequence $(a_1, a_2, \ldots.)$ of A such that $a_n \to a$ in $T_0(E; F)$, *i.e.*, $|f_i(a_n) - f_i(a)| \to 0$ as $n \to \infty$ for each $i = 1, 2, \ldots.$, by using the expression for the metric $\rho(\alpha, \beta)$ given in theorem 4. Hence to complete the proof of the theorem it is enough to show that there exists a sequence of increasing positive integers $(p_1, p_2, \ldots.)$ such that $\max_{1 \leqslant i < \infty} \frac{|f_i(a_n - a)|}{p_i} \to 0$ as $n \to \infty$.

Putting $\epsilon_{ni} = |f_i(a_n - a)|$, the proof of the following lemma will complete the proof of theorem 5.

LEMMA 5.—*Let ϵ_{ni}, $n, i = 1, 2, \ldots.$, be a double sequence of non-negative numbers that $\epsilon_{ni} \to 0$ as $n \to \infty$ for each $i = 1, 2, \ldots.$ Then there exists a sequence of increasing positive integers $(p_1, p_2, \ldots.)$ such that*

$$\epsilon_n = \max_{1 \leqslant i < \infty} \frac{\epsilon_{ni}}{p_i} \to 0 \text{ as } n \to \infty.$$

Proof.—Since $\epsilon_{ni} \to 0$ as $n \to \infty$ for each $i = 1, 2, \ldots.$ the number $\mu_i = \max_{1 \leqslant n < \infty} \epsilon_{ni}$ is finite. Let ν_i = the integer next to max $(\mu_1, \mu_2, \ldots. \mu_i)$ and $p_i = i\nu_i$ for $i = 1, 2, \ldots.$ Given the positive integer k, we can find an integer n_k such that $\epsilon_{ni} \leqslant \frac{1}{k}$ for $n \geqslant n_k$ and $i = 1, 2, \ldots. k$. Let $n \geqslant n_k$. Then $\max_{1 \leqslant i \leqslant k} \frac{\epsilon_{ni}}{p_i} \leqslant \frac{1}{k}$. Also if $i > k$ we have $\frac{\epsilon_{ni}}{p_i} \leqslant \frac{\epsilon_{ni}}{i\nu_i} \leqslant \frac{1}{k}$. Hence $\epsilon_n = \max_{1 \leqslant i < \infty} \frac{\epsilon_{ni}}{p_i} \leqslant \frac{1}{k}$ for $n \geqslant n_k$. Hence $\epsilon_n \to 0$ as $n \to \infty$; so the lemma is proved.

3.4. *On the Cardinal Number of the set RN (E; F).*—By theorem 5, the set RN (E; F) is more than enumerable. Since each topology in RN (E; F) is determined by a sequence of integers, the cardinal number of RN (E; F) does not exceed that of the continuum. More precisely we can assert that the cardinal number of the set RN (E; F) is exactly that of the continuum. For each x in $1 \leqslant x \leqslant 2$ the sequence $p_n(x) = [n^x]$ where $[t]$ denotes the integral part of t, gives a topology of RN (E; F) and for different x, we get different topologies as may be seen by using lemma 2. Hence the cardinal number of RN (E; F) is exactly that of the continuum. But all the same we cannot assert that the least cardinal number of the set of topologies of RN (E; F) required to get T_0 (E; F) as a lattice-product is precisely that of the continuum. For instance the topologies corresponding to $\{p_n(x)\}$, $1 \leqslant x \leqslant 2$ can be replaced by (e^n) so far as the lattice product is concerned.

3.5. The following general theorem seems to throw some light on the result of theorem 4.

THEOREM 6. *Let E be a linear space and $N_1 > N_2 > N_3 \ldots$. be a strictly decreasing infinite sequence of normed topologies on E. Then the lattice product T of $(N_1, N_2, \ldots)$ is not normable.*

Proof.—Let $|\alpha|_i$ denote the norm of α in N_i. By using lemma 1, we can so choose these norms (note that $|\alpha|$ and $k|\alpha|$ are equivalent norms) that the inequalities

$$|\alpha| \geqslant |\alpha|_2 \geqslant |\alpha|_3 \ldots. \tag{7}$$

are satisfied for all $\alpha \epsilon E$. Suppose if possible that T is normable. Let $|\alpha|$ be the norm. As in the proof of lemma 1 we can find a sequence $(\alpha_{i1}, \alpha_{i2} \ldots.)$ such that

$$|\alpha_{in}| \to 0 \text{ as } n \to \infty \text{ while } |\alpha_{in}|_i = 1 \text{ for all } n \tag{8}$$

and for each $i = 1, 2, \ldots..$ Now by induction we can choose $\alpha_i = \alpha_{ip_i}$ such that $|\alpha_{ip_i}| \leqslant \frac{1}{i}, = 1, 2, \ldots..$ Now the Set $A = (\alpha_1, \alpha_2 \ldots.)$ is closed in each N_i, $i = 1, 2 \ldots$ because for a given i, $|\alpha_n|_i \geqslant |\alpha_{np_n}|_n = 1$ for $n \geqslant i$) but it is not closed in T because Θ is a point of $(\bar{A})_T$ not belonging to A. This contradiction proves the theorem.

Remark.—It would be interesting to find out if the dual of this result is true. Also whether the theorem is true for *any infinite collection* of normed topologies.

3.6. As an illustration of theorem 7, consider the space L_p of functions pth power of whose modulus is summable on a set X of finite measure. Then $L_p \supset L_q$ if $q > p$ and the norm $\{\int_X |f|^p\}^{\frac{1}{p}}$ defines a stronger topology on L_q than the norm $\{\int_X |f|^q\}^{\frac{1}{q}}$. Let $r_1 > r_2 > \ldots\ldots$ be a sequence converging to p. Let E be the linear space L_{r_1}, and N_{r_i} the topology on E induced by the norm $\{\int_X |f|^{r_i}\}^{\frac{1}{r_i}}$. Then $N_{r_1} > N_{r_2} > \ldots\ldots$ is a strictly decreasing sequence of normed topologies on E. It would be natural to expect that N_p is the lattice product of the set $\{N_{r_i}\}$ but the above theorem shows that it is not and that the lattice product is weaker than N_p.

4 We shall conclude with a few illustrations of theorems 5 and 6.

(1) Let C denote the linear space of all real number sequences $\alpha = (a_1\, a_2, \ldots\ldots)$ such that $S_0(\alpha) = \sum_1^\infty a_n$ converges. Let F denote the total family of functionals $S_0(\alpha)$, $S_i(\alpha) = \sum_1^i a_n$, $i = 1, 2, \ldots\ldots$ The norm $\max_{0 \leqslant n < \infty} |S_n(\alpha)| = |\alpha|$ is such that the functionals of F are continuous in $N(C; |\alpha|)$. So the results of theorems 5 and 6 hold for the topology $T_0(C; F)$ on C.

(2) Let E denote the linear space of functions $\alpha = \alpha(t)$ integrable in (0, 1) in any given sense (*e.g.*, Reimann, Lebesque, or Denjoy). Let F denote the family of functionals $f_x(\alpha) = \int_0^x \alpha(t)\, dt$, $0 \leqslant x \leqslant 1$. *The corresponding space $T_0(E; F)$ is not metrisable.* To see this, suppose $T_0(E; F)$ is metrisable. Then we can find an enumerable system $(U_1, U_2, \ldots\ldots)$ of neighbourhoods of $\Sigma(\Theta)$ such that any $U \in \Sigma(\Theta)$ contains one U_i. Now by the definitions of $U_i \in \Sigma(\Theta)$ we see that at most an enumerable set of functionals of F are exhausted in the definitions of the set $(U_1, U_2, \ldots\ldots)$. Hence there exists a sequence of numbers $(r_1, r_2, \ldots\ldots)$ such that the functionals $f_{r_i}(\alpha) = \int_0^{r_i} \alpha(t)\, dt$ are precisely the functionals appearing in the definitions of $(U_1, U_2, \ldots\ldots)$. So we can find x in (0, 1) different from each of $(r_1, r_2, \ldots\ldots)$. Now we shall show that there exists no $U_i \subset U(f_x; 1)$. Let U_i be defined by the relations

$$|f_{r_i}(\alpha)| < \delta,\ i = 1, 2, \ldots\ldots|,$$

where $r_1 < r_2 < \ldots . < r_p$. Define $\alpha(t)$ as follows:

$$\alpha(t) = 2/x \text{ in } 0 \leqslant t \leqslant x \text{ and } = 0 \text{ otherwise if } x < r_1;$$

$$= \frac{2}{x - r_i} \text{ in } r_i \leqslant t < x; = \frac{-2}{r_{i+1} - n} \text{ in } x \leqslant t \leqslant r_{i+1} \text{ and } = 0$$

otherwise if $r_i < x < r_{i+1}$;

$$= \frac{2}{x - r_p} \text{ in } r_p < t < x \text{ and } = 0 \text{ otherwise if } x > r_p.$$

Then $\int_0^n \alpha(t)\, dt = 2$ while $\int_0^{r_i} \alpha(t)\, dt = 0$, $i = 1, 2, \ldots . p$. Hence $\alpha \in U_i$ but not in U. So $T_0(E; F)$ is not metrisable.

5.1. I understand from a referee that theorem 1 is classical and theorems 2 and 3 are known.[11] These results are still kept here for the sake of completeness.

[11] G. W. Mackey "On Convex Topological Linear Spaces," *Proc. Nat. Acad. Sci.*, 1943, **29**, 315–319, theorems 4 and 3.

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